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HARPER'S SCIENTIFIC MEMOIRS

EDITED BY

J. S. AMES, PH.D.

PROFESSOR OF PHYSICS IN JOHNS HOPKINS UNIVERSITY

IV.

THE MODERN THEORY OF SOLUTION

THE MODERN THEORY OF SOLUTION

MEMOIRS BY PFEFFER, VAN'T HOFF ARRHENIUS, AND RAOULT

TRANSLATED AND EDITED

By HARRY C. JONES, Ph.D.

ASSOCIATE IN PHYSICAL CHEMISTRY IN JOHNS HOPKINS UNIVERSITY

NEW YORK AND LONDON

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PREFACE

It is well known that great progress has been made in physical chemistry during the last ten or fifteen years. Indeed, this has been of such a character that what is now studied and taught under the head of physical chemistry differs fundamentally from what was included under that subject a few decades ago.

The papers in this volume have been selected and arranged with the idea of showing how the two leading generalizations, which underlie these recent developments, have been reached. Previous to 1885, physical chemistry dealt chiefly with the physical properties of chemical substances, and the relations between properties and composition on the one hand, and properties and constitution on the other. How would the difference in composition of an oxygen atom, or a CH_2 group, affect the physical properties, or what would be the effect of an oxygen atom united to hydrogen with respect to an oxygen atom united to carbon, were questions which investigators were endeavoring to answer.

The first important advance was made possible by the work of the botanist Pfeffer. He undertook to investigate the osmotic pressure which solutions of substances exert against the pure solvent. His work, which was published in an extensive monograph, *Osmotische Untersuchungen,* was carried out purely from a physiological-botanical stand-point, and Pfeffer did not indicate its bearing upon any physical-chemical problem. Enough of his work is given to show the method which he used and the apparatus which he employed. He worked with solutions of several substances in water, but from our point of view it is important to note that he worked with different dilutions of the same substance in the same solvent, and

also determined the temperature coefficient of osmotic pressure. Just enough of his results are given to bring out these two important points.

The paper of Van't Hoff, given in full in this volume, was published in the first volume of the *Zeitschrift für Physikalische Chemie* in 1887. In this, the relation between dilute solutions and gases was pointed out for the first time. The law of Boyle for gas-pressure was found to be applicable to the osmotic pressures of solutions of different concentrations. That osmotic pressure is proportional to concentration was found to be true from the results of Pfeffer's investigations. This was the first important generalization showing the relation between gases and dilute solutions.

Van't Hoff showed, further, from Pfeffer's results, as well as theoretically, that the law of Gay-Lussac for the temperature coefficient of gas-pressure, applies to the temperature coefficient of osmotic pressure, which was the second important step. Then Van't Hoff took another and even more important step, showing that the osmotic pressure of a dilute solution is exactly equal to the gas-pressure of a gas at the same temperature, containing the same number of molecules in a given space as there are molecules of dissolved substance. Thus, two grams of hydrogen ($H_2=2$) will exert a gas-pressure in a space of a litre which is exactly equal to the osmotic pressure which three hundred and forty-two grams of cane-sugar ($C_{12}H_{22}O_{11} = 342$) will exert in a litre of aqueous solution. From this, the law of Avogadro for gases applies at once to dilute solutions, and we can then say that solutions having the same osmotic pressure, at the same temperature, contain the same number of ultimate parts in unit space.

Thus, the three fundamental laws of gas-pressure apply to the osmotic pressure of dilute solutions, and we are therefore justified in attempting to apply other laws of gases to dilute solutions. We have said dilute solutions, and have thus indicated that the gas laws would not apply to concentrated solutions. This is true, and in this, again, solutions are analogous to gases, since the ordinary gas laws do not apply to very concentrated gases—*i. e.*, gases near the point of liquefaction.

But if the laws of gas-pressure apply to the osmotic pressure of dilute solutions, then we would naturally ask if any exceptions to the laws of gas-pressure find their counterpart in the

osmotic pressure of solutions. We know that certain vapors, as that of ammonium chloride, exert a greater pressure than they would be expected to do from Avogadro's law. These vapors, then, are exceptions to the gas laws.

We find their strict analogues in the osmotic pressures of certain solutions. The laws of gas-pressure apply to the osmotic pressures of dilute solutions of substances of the class of cane-sugar—*i. e.*, those substances whose solutions do not conduct the electric current. As quickly as we turn to solutions of the strong acids and bases, and salts, we find that all of them, when dissolved in water, exert an osmotic pressure against the water which is greater than would be calculated from the concentration. Just as the vapor-pressure of ammonium chloride is abnormally large, so the osmotic pressure of solutions of substances such as those named above is abnormally large. The gas laws not only apply to the osmotic pressure of solutions, but just as there are exceptions to these laws in gas-pressure, so, also, there are exceptions in osmotic pressure.

What is the explanation of these apparent anomalies? This phenomenon was, for a long time, unexplained for gases. It was pointed out that here were exceptions to the law of Avogadro, and this law could, therefore, not be generally applicable. But the anomalies were finally accounted for with gases by showing that vapors like those of ammonium chloride dissociated or broke down into constituent parts, the amount of the dissociation depending in part upon the temperature. That the vapor of ammonium chloride is partly broken down into ammonia and hydrochloric acid was shown, in a perfectly satisfactory manner, by the work of Pebal and others.

But of what aid was this explanation for anomalous gas-pressure, in ascertaining the cause of the abnormal osmotic pressure of dilute solutions of acids, bases, and salts? It was simple enough to conceive of a molecule of ammonium chloride being broken down by heat as follows:

$$NH_4Cl = NH_3 + HCl,$$

especially after it had been proven experimentally that the vapor of ammonium chloride contains both free ammonia and free hydrochloric acid; and this increase in the number of parts present would explain the abnormally large gas-pressure, and still allow the law of Avogadro to be generally applicable.

But could we conceive of any analogous explanation for the abnormal osmotic pressures? How could water break down stable compounds, such as the strong acids and bases? Arrhenius explained these abnormal osmotic pressures in a paper published also in the first volume of the *Zeitschrift für Physikalische Chemie*, and which is also given in full in this volume. According to him, those substances which give abnormally large osmotic pressures are broken down in solution, not into molecules as ammonium chloride is broken down into molecules by heat, but into ions, which are atoms, or groups of atoms, charged with electricity. It is very important in this connection to distinguish between atoms and ions. A compound like potassium chloride is, according to Arrhenius, broken down, or, as he would say, dissociated into potassium ions and chlorine ions, which exist in the presence of water. If a potassium ion had properties at all similar to a potassium molecule the suggestion of Arrhenius would be absurd, since it is well known how vigorously ordinary potassium acts upon water, while potassium chloride dissolves in water without any such action. The fundamental distinction between molecules and ions is that the latter are charged either positively or negatively, and by virtue of their charge do not have properties similar to those of the molecules.

This assumption, that the molecules of those substances which give abnormally large osmotic pressures are broken down in solution into a larger number of parts, if true, shows that the law of Boyle holds for the osmotic pressure of all dilute solutions—*i. e.*, the osmotic pressure is proportional to the number of parts present. In the case of those substances whose solutions do not conduct the current—non-electrolytes—the molecules exist in solution as such, and each exerts its own definite osmotic pressure. But in solutions of those substances which conduct the current, at least some of the molecules are broken down into ions, the number depending upon the dilution, and each ion exerts just the same osmotic pressure as a molecule. Since a molecule cannot break down into less than two ions, those substances whose solutions are even partly dissociated into ions must exert greater osmotic pressure than those whose solutions are completely undissociated.

The suggestion that solutions of electrolytes contain ions which conduct the current is not new with Arrhenius.

Grotthuss attempted to explain how the current is able to pass through a solution of an electrolyte, and Clausius assumed the presence of free ions in electrolytic solutions. The chemist Williamson, as the result of his now classic synthesis of ether, also concluded that molecules of substances are broken down in solution. But the application of electrolytic dissociation, as it is called, to explain the abnormally large osmotic pressures of electrolytes, we owe to Arrhenius. And what is even more important, he did not simply assume that solutions of electrolytes are partly broken down or dissociated into ions, but showed how the amount of such dissociation could be measured quantitatively.

It was found that those substances which give abnormally large osmotic pressures, give abnormally great depressions of the freezing-point of the solvent, and, further, solutions of such substances conduct the current. Arrhenius showed that if the assumption of electrolytic dissociation to account for abnormally large osmotic pressures was true, then it must also account for the abnormally large depressions of the freezing-point. The amount of dissociation of a given solution, calculated from its osmotic pressure, should then agree with the dissociation calculated from the lowering of the freezing-point. But since direct measurements of osmotic pressure will be seen from Pfeffer's work to be difficult, this comparison could not be made directly.

But if Arrhenius's theory of electrolytic dissociation is true, then it must account for the property of solutions to conduct the current; and since conductivity is due only to ions, the amount of conductivity could be used to measure the amount of dissociation. Arrhenius did not compare the dissociation as calculated from the freezing-point lowerings, directly with that calculated from conductivity, but compared the values of a certain coefficient, i, obtained by the two methods for a large number of substances, and found a striking agreement throughout. This agreement, then, made it probable that the theory of electrolytic dissociation corresponds to a great truth in nature, and that the analogy between solutions and gases is even more deeply seated than was at first supposed.

It is impossible to show here the wide-reaching significance of this analogy, and of the theory of electrolytic dissociation. This would require a fairly comprehensive survey of the field of

physical chemistry. Suffice it to say here that all of the more important advances in physical chemistry during the last ten or twelve years have centred around these two generalizations, which may be termed the corner-stones of modern physical chemistry.

It has already been stated that those substances which give abnormally large osmotic pressures, give abnormally great depressions of the freezing-point of the solvent. This brings us to the work of Raoult on the freezing-point depression, and lowering of vapor-tension, of solvents by substances dissolved in them. Three of the more important papers of Raoult along these lines are given in this volume.

Raoult showed that the depression of the freezing-point of a solvent, or of its vapor-tension, depends upon the relation between the number of molecules of solvent and of dissolved substance. He showed from this how it was possible to determine the unknown molecular weights of substances, by determining how much a given weight of the substance would lower the freezing-point, or lower the vapor-tension, of a given weight of a solvent in which it was dissolved. These methods, the theoretical development of which we owe to Raoult, have been greatly improved by others from an experimental stand-point, and have been very widely applied, especially to the determination of the molecular weights of substances. It should be especially mentioned that the method of measuring the depression of the vapor-tension has been almost entirely supplanted by the method of determining the temperature at which solvent and solution boil. From the rise in the boiling-point of the solvent produced by the dissolved substance we can calculate the molecular weight of the latter. This improvement on the Raoult method of measuring the depression in vapor-tension we owe to Beckmann.

The freezing-point method especially has now been improved until it can be also used as a fairly accurate measure of electrolytic dissociation. And it can be stated that electrolytic dissociation, measured by the freezing-point method, agrees within the limits of experimental error, with that measured by the conductivity method.

The following papers will show, then, how the analogy between dilute solutions and gases was first recognized and pointed out, and how the theory of electrolytic dissociation arose to

account for the abnormal results obtained with electrolytes—abnormally large osmotic pressures, depressions of freezing-point, and depressions of vapor-tension.

Since the theory was proposed it has been tested both theoretically and experimentally from many sides; with the result that, when all of the evidence available is taken into account, the theory of electrolytic dissociation seems to be as well established as many of our so-called laws of nature.

HARRY C. JONES.

Johns Hopkins University.

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OSMOTIC INVESTIGATIONS

BY

DR. W. PFEFFER

Professor of Botany in the University of Leipsic

SELECTED SECTIONS

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OSMOTIC INVESTIGATIONS*

BY

DR. W. PFEFFER

SELECTED SECTIONS

A.—APPARATUS AND METHOD

1.—PREPARATION OF THE CELLS

CERTAIN precipitates can be obtained as membranes if they are formed at the plane of contact of two solutions, or of a solution and a solid. Traube, as is known, was the first to prepare such membranes, and he, at the same time, worked out the conditions under which they can be formed, conditions which later will be briefly explained. The author of this important discovery tested membranes obtained from different substances as to their permeability to dissolved bodies; and it was shown that substances in general pass less easily through such membranes than through those formerly employed in diosmotic investigations. Indeed, many substances which easily diosmose through the latter were incapable of passing through definite precipitated membranes.

Traube carried out diosmotic investigations, for the most part, with membranes which closed one end of a glass tube, into which the substance whose diosmotic properties were to be tested was introduced. Such an apparatus is, in most cases, easily prepared; a small quantity of one of the solutions necessary to produce a precipitate being introduced into the glass

* Selected paragraphs from Pfeffer's *Osmotische Untersuchungen*, Leipsic, 1877.

tube, which is then dipped into the other solution. With correct procedure, the precipitate is formed as a membrane closing the tube, at the surface where the solutions of the two "membrane-formers" come in contact.

Traube worked in every case with cells protruding free into the liquid. These are, on the one hand, not very resistant; and, further, they continually increase in size as long as an osmotic current of water flowing in produces a pressure in the interior which tends to distend the membrane. By this means a new membrane particle is inserted as soon as the two membrane-formers meet in the enlarged interstices—an increase in surface by intussusception which these membranes very beautifully demonstrate. But even if it were possible to overcome these and other difficulties when the problem is to study diosmotic exchange, yet it is impossible, in freely suspended cells, to measure the pressure brought about by osmotic action. To render this possible the membranes must be placed against a support, which can offer resistance to ordinary pressure, but which is relatively easily permeable to water and salts. The plant cells furnish us with the model desired for imitation. In these the plasma membrane, which, in its diosmotic properties, is similar to the artificially precipitated membranes, is pressed against the cell wall.

In my first experiments, freely suspended membranes were allowed to increase by osmotic pressure until they finally rested on a support which closed one end of a glass tube. If, finally, with some trouble, this was accomplished, other difficulties appeared, in reference to measurement of pressure, which induced me to adopt another course. The precipitated membrane, even under slight pressure, would be squeezed through the pores even of the thickest linen and silken textures—*i. e.*, the continually growing membrane appeared on the other side of the texture, in different places, in the form of small sacs, which further increased in size and finally burst.

Attempts to use thicker material as supports, such as parchment paper or porcelain cells, did not yield favorable results, for reasons which I shall leave undiscussed here.

I obtained the first favorable result by proceeding as follows: I took [*unglazed*] porcelain cells, such as are used for electric batteries, and, after suitably closing them, I first injected them carefully with water, and then placed them in a solution of cop-

per sulphate, while, either immediately or after a short time, I introduced into the interior a solution of potassium ferrocyanide. The two membrane-formers now penetrate diosmotically the porcelain wall separating them, and form, where they meet, a precipitated membrane of copper ferrocyanide. This appears, by virtue of its reddish-brown color, as a very fine line in the white porcelain which remains colorless at all other places, since the membrane, once formed, prevents the substances which formed it from passing through.

These membranes, deposited in the interior of porcelain walls, I have used, moreover, almost exclusively for preliminary experiments, the investigation proper being carried out with membranes which were deposited on the inner surface of porcelain cells. All the experiments to be described are carried out with the latter kind of membranes, if not especially stated to be otherwise. To prepare these, the porcelain cells were completely injected with, *e. g.*, a solution of copper sulphate, then quickly rinsed out with water, and a solution of potassium ferrocyanide afterwards added. More minute details as to the preparation of the apparatus will be given later, after this general account.

In Fig. 1, the apparatus ready for use, with the manometer (m) for measuring the pressure, is shown, at approximately one-half the natural size. The porcelain cell (z) and the glass pieces v and t, inserted in position, are shown in median longitudinal section. The porcelain cells which I used were, on an average, approximate-

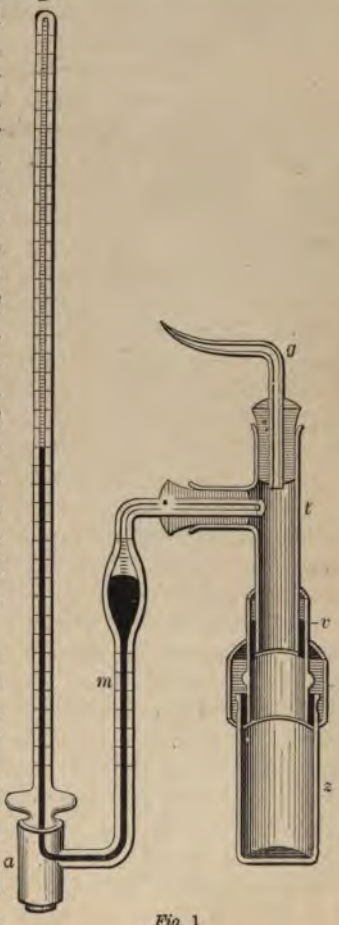

Fig. 1

ly 46 millimetres high, were about 16 millimetres' internal diameter, and the walls were from 1¼ to 2 millimetres thick. The narrow glass tube *v*, called the connecting-piece, was fastened into the porcelain cell with fused sealing-wax, and the closing piece *t* was set into the other end of this tube in the same manner. The shape and purpose of this are shown in the figure. The glass ring *r* was necessary only in experiments at higher temperature, in which the sealing-wax softened. The ring was then filled with pitch, which also held together firmly the pieces inserted into one another.

[*Two pages omitted.*]

All porcelain cells were treated first with dilute potassium hydroxide, then with dilute hydrochloric acid (about 3 per cent.), and, after being well washed, were again completely dried, before they were closed as already described. Substances which are soluble in these reagents, such as oxides and iron, which under certain conditions can do harm, would thus be removed.

After the apparatus was closed, the precipitated membrane was formed, either in the wall or upon the surface, according to the principle already indicated. In order that this should be done successfully, a number of precautionary measures are necessary, and these will now be discussed. Since I experimented chiefly with membranes of copper ferrocyanide, which were deposited upon the inner surface of porcelain cells, I will fix attention especially upon this case.

The porcelain cells were first completely injected with water under the air-pump, and then placed, for at least some hours, in a solution containing 3 per cent. of copper sulphate, and the interior was also filled with this solution. The interior only of the porcelain cell was then once rinsed out quickly with water, well dried as quickly as possible, by introducing strips of filter paper, and after the outside had dried off somewhat it was allowed to stand some time in the air until it just felt moist. Then a 3-per-cent. solution of potassium ferrocyanide was poured into the cell, and this immediately reintroduced into the solution of copper sulphate.

After the cell had stood for from twenty-four to forty-eight hours undisturbed, it was completely filled with the solution of potassium ferrocyanide, and closed as shown in Fig. 1. A certain excess of pressure of the contents of the cell now

gradually manifested itself, since the solution of potassium ferrocyanide had a greater osmotic pressure than the solution of copper sulphate. After another twenty-four to forty-eight hours the apparatus was again opened, and generally a solution introduced which contained 3 per cent. of potassium ferrocyanide and 1½ per cent. of potassium nitrate (by weight), and which showed an excess of osmotic pressure of somewhat more than three atmospheres. If the cell should, moreover, be used for experiments in which a higher pressure was produced, it was also tested at a higher pressure by using a solution richer in potassium nitrate. In these test experiments, of course, any home-made manometers can be used.

[*Eleven pages omitted.*]

4.—MEASUREMENT OF THE PRESSURE

The osmotic pressures were measured chiefly with air-manometers, open manometers being applicable only where smaller pressures were involved. The form of my air-manometer is shown in Fig. 1, in approximately half its natural size. The longer closed limb is connected with the shorter open limb by means of the glass cock already mentioned. An enlargement is blown upon the shorter limb for the reception of mercury. There is a millimetre scale upon both limbs, starting from the same zero point. The scale upon the closed arm is 200 millimetres in length. This arm was selected of small diameter (in the three manometers which I employed it was between 1.166 and 1.198 millimetres), so that the osmotic pressure can be established more quickly, and without any considerable amount of water entering the apparatus. The diameter of the arm, bent twice at right angles, was larger throughout, and was from 7.5 to 8 millimetres in the enlarged space.

[*One page omitted.*]

In use, the space in the open arm of the manometer which was not filled with mercury, was filled with the liquid whose osmotic action was to be tested. The cell was then also filled with this, after the manometer was attached, as shown in Fig. 1, and then the final closing made without leaving any air in the apparatus, in the manner already given, with the aid of a glass tube drawn out to a capillary. After the capillary point is melted off, it is recommended to produce

some pressure in the cell, by pushing the glass tube farther in, in order to lessen the time required to reach the final pressure, and at the same time to diminish the amount of water which enters the apparatus. The apparatus can be opened again without any difficulty, after the experiment is over, by blowing open the capillary point in the flame. If the form of the glass tube *t* allows the rubber corks to expand somewhat at their inner ends, they acquire thus a considerable support. Yet, for higher pressures, they were always secured by tying them down with metal wire (copper or silver wire), as champagne bottles are closed. I have been able to close the apparatus easily, so that it would withstand, perfectly, a pressure of seven atmospheres.

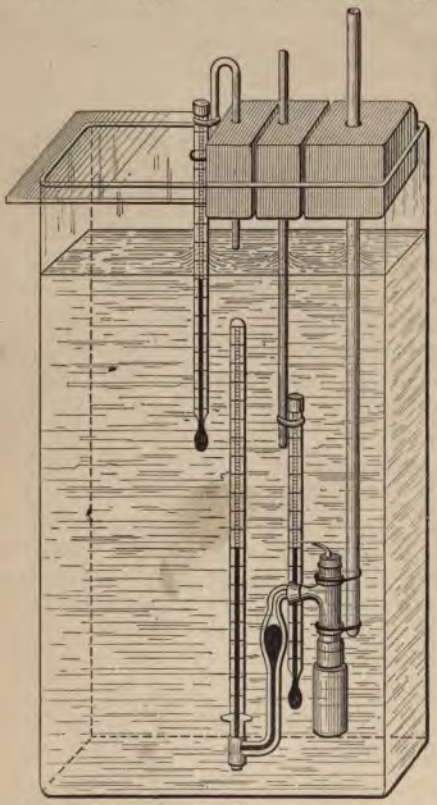

Fig. 2

The closed cell, as seen in Fig. 2, is fastened to a glass rod passing through a cork, and was introduced into a bath in such a manner that the manometer, as well, was entirely immersed in the liquid. The temperature was measured by two accurate thermometers. By covering that portion of the bath not closed with corks with a brass plate, evaporation of the liquid was diminished when the bath was filled with a dilute solution of a membrane-former. The apparatus is represented in the figure at approximately one-fourth its natural size. The baths held from 2 to 2½ litres of liquid.

It is best to place the baths in dishes filled with sand, in order that the manometers may be easily adjusted with accuracy to a vertical position. If the entire apparatus is covered with a bell-jar, and kept in a room of uniform temperature, it is not difficult to keep the thermometers constant for several hours to within less than $\frac{1}{10}°$. This constancy of temperature is of significance, because the final condition of equilibrium between the osmotic inflow and filtration under pressure is established very slowly, especially at low temperatures, and therefore, before the experiment is completed, we are compelled to assure ourselves that the mercury stands at the same height in the manometer for several hours.

In determining osmotic pressures at higher temperatures, the entire vessel was placed in a heating apparatus which was filled with sand and covered with a bell-jar, and whose temperature was accurately regulated. Care must be taken, in passing from lower to higher temperatures, that the junctions of the apparatus are not injured by the increased pressure which is caused by the expansion of liquid and air.

Small osmotic pressures were, indeed, measured with an open manometer, whose longer arm was made of a narrow tube of approximately 0.3 millimetre diameter, in order that the condition of equilibrium might be quickly reached. The form and method of using this manometer requires no special explanation. It should be observed, in passing, that the error of measurement is, in any case, less than 3 millimetres.

[*Thirteen sections omitted.*]

17.—EXPERIMENTAL RESULTS

NO. VII.

Pressures for Cane-Sugar of Different Concentration.

CONCENTRATION IN PER CENT. BY WEIGHT.	PRESSURE.
1	535 mm.
2	1016 "
2.74	1518 "
4	2082 "
6	3075 "
1	535 "

Surface of membrane, 17.1 square centimetres.

TABLE 12*

EXPERIMENTS WITH A ONE-PER-CENT. SOLUTION OF CANE-SUGAR

[*Change in Osmotic Pressure with Change in Temperature.*]

	TEMPERATURE.	PRESSURE.
a	14.2° C.	51.0 cm.
	32.0° C.	54.4 "
b	6.8° C.	50.5 cm.
	13.7° C.	52.5 "
	22.0° C.	54.8 "
c	15.5° C.	52.0 cm.
	36.0° C.	56.7 "

WILHELM FRIEDRICH PHILIPP PFEFFER was born March 9th, 1845, at Grebenstein, Cassel. He received the Degree of Doctor of Philosophy at Göttingen in 1865, was appointed Privatdocent in Marburg in 1871, and in 1873 was elected to a subordinate professorship in Bonn. He became professor in Basel in 1877, and was called to Tübingen in 1878. He is at present Professor of Botany in the University of Leipsic. Some of his more important papers, in addition to his investigations of osmotic pressure, are: *Physiological Investigations*, Leipsic, 1873; *Action of the Spectrum Colors on the Decomposition of Carbon Dioxide in Plants; Studies on Symmetry and the Specific Causes of Growth; Plant Physiology*, Vol. I., 1881; *Construction of a Number of Pieces of Apparatus for Investigating the Growth of Plants.* His measurements of osmotic pressure are, with perhaps one slight exception, the only direct measurements which have been made up to the present.

* *Osmotische Untersuchungen*, p. 85.

THE RÔLE OF OSMOTIC PRESSURE IN THE ANALOGY BETWEEN SOLUTIONS AND GASES

BY

J. H. VAN'T HOFF

Professor of Physical Chemistry in the University of Berlin

(*Zeitschrift für Physikalische Chemie*, I., 481, 1887)

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THE RÔLE OF OSMOTIC PRESSURE IN THE ANALOGY BETWEEN SOLUTIONS AND GASES*

BY

J. H. VAN'T HOFF

In an investigation, whose essential aim was a knowledge of the laws of chemical equilibrium in solutions,† it gradually became apparent that there is a deep-seated analogy—indeed, almost an identity—between solutions and gases, so far as their physical relations are concerned; provided that with solutions we deal with the so-called osmotic pressure, where with gases we are concerned with the ordinary elastic pressure. This analogy will be made as clear as possible in the following paper, the physical properties being considered first:

1.—OSMOTIC PRESSURE. KIND OF ANALOGY WHICH ARISES THROUGH THIS CONCEPTION.

In considering the quantity, with which we shall chiefly have to deal in what follows, at first from the theoretical point of view, let us think of a vessel, A, completely filled, for example, with an aqueous solution of sugar, the vessel being placed in water, B. If, now, the perfectly solid wall of the vessel is permeable to water, but impermeable to the dissolved sugar, the attraction of the water by the solution will, as is well known, cause the water to enter A, but this action will soon reach its limit due to the pressure produced by the water which enters (in minimal quantity). Equilibrium exists under these

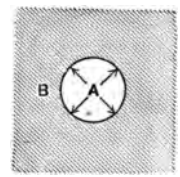

Fig. 1

* *Ztschr. Phys. Chem.*, **1**., 481, 1887.

† *Études de Dynamique Chimie*, 179; *Archives Néerlandaises*, **20**; *k. Svenska Akademiens Handl.*, **21**.

conditions, and the pressure exerted on the wall of the vessel we will designate in the following pages as osmotic pressure.

It is evident that this condition of equilibrium can be established in A also at the outset, that is, without previous entrance of water, by providing the vessel B with a piston which exerts a pressure equal to the osmotic pressure. We can then see that by increasing or diminishing the pressure on the piston it is possible to produce arbitrary changes in the concentration of the solution, through movement of water in the one or the other direction through the walls of the vessel.

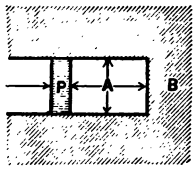

Fig. 2

Let this osmotic pressure be described from an experimental stand-point by one of Pfeffer's* experiments. An unglazed porcelain cell was used, which was provided with a membrane permeable to water, but not to sugar. This was obtained as follows: The cell, thoroughly moistened, so as to drive out the air, and filled with a solution of potassium ferrocyanide, was placed in a solution of copper sulphate. The potassium and copper salts came in contact, after a time, by diffusion, in the interior of the porous wall, and formed there a membrane having the desired property. Such a vessel was then filled with a one-per-cent. solution of sugar, and, after being closed by a cork with manometer attached, was immersed in water. The osmotic pressure gradually makes its appearance through the entrance of some water, and after equilibrium is established it is read on the manometer. Thus, the one-per-cent. solution of sugar in question, which was diluted only an insignificant amount by the water which entered, showed, at 6.8°, a pressure of 50.5 millimetres of mercury, therefore about $\frac{1}{15}$ of an atmosphere.

The porous membranes here described will, under the name "semipermeable membranes," find extensive application in what follows, even though in some cases the practical application is, perhaps, still unrealized. They furnish a means of dealing with solutions, which bears the closest resemblance to that used with gases. This evidently arises from the fact that the elastic pressure, characteristic of the latter condition, is now introduced also for solutions as osmotic pressure. At the

* *Osmotische Untersuchungen*, Leipsic, 1877.

same time let stress be laid upon the fact that we are not dealing here with an artificially forced analogy, but with one which is deeply seated in the nature of the case. The mechanism by which, according to our present conceptions, the elastic pressure of gases is produced is essentially the same as that which gives rise to osmotic pressure in solutions. It depends, in the first case, upon the impact of the gas molecules against the wall of the vessel; in the latter, upon the impact of the molecules of the dissolved substance against the semipermeable membrane, since the molecules of the solvent, being present upon both sides of the membrane through which they pass, do not enter into consideration.

The great practical advantage for the study of solutions, which follows from the analogy upon which stress has been laid, and which leads at once to quantitative results, is that the application of the second law of thermodynamics to solutions has now become extremely easy, since reversible processes, to which, as is well known, this law applies, can now be performed with the greatest simplicity. It has been already mentioned above that a cylinder, provided with semipermeable walls and piston, when immersed in the solvent, allow any desired change in concentration to be produced in the solution beneath the piston by exerting a proper pressure upon the piston, just as a gas is compressed and can then expand; only that in the first case the solvent, in these changes in volume, moves through the wall of the cylinder. Such processes can, in both cases, preserve the condition of reversibility with the same degree of ease, provided that the pressure of the piston is equal to the counter-pressure, *i. e.*, with solutions, to the osmotic pressure.

We will now make use of this practical advantage, especially for the investigation of the laws which hold for "ideal solutions," that is, for solutions which are diluted to such an extent that they are comparable with "ideal gases," and in which, therefore, the reciprocal action of the dissolved molecules can be neglected, as also the space occupied by these molecules, in comparison with the volume of the solution itself.

2.—BOYLE'S LAW FOR DILUTE SOLUTIONS.

The analogy between dilute solutions and gases acquires at once a more quantitative form, if we consider that in both

cases the change in concentration exerts a similar influence on the pressure; and, indeed, the values in question are, in both cases, proportional to one another.

This proportionality, which for gases is designated as Boyle's law, can be shown for osmotic pressure, experimentally from data already at hand, and also theoretically.

Experimental Proof. Determination of the Osmotic Pressure at Different Concentrations.—Let us first give the results of Pfeffer's determinations* of osmotic pressure (P) in solutions of sugar, at the same temperature (13.2°–16.1°) and different concentrations (C):

C	P	$\frac{P}{C}$
1%.....	535 mm.....	535
2%.....	1016 "	508
2.74%.....	1518 "	554
4%.....	2082 "	521
6%.....	3075 "	513

The nearly constant value of $\frac{P}{C}$ indicates that, in fact, a proportionality between pressure and concentration exists.

Experimental Proof. Comparison of Osmotic Pressure by Physiological Methods.—The observations of De Vries† can be placed with the above as a second line of evidence. From these it follows that equal changes in concentration of solutions of sugar, potassium nitrate, and potassium sulphate, exert the same influence on the osmotic pressure. The above-named investigator compared, by physiological methods, the osmotic pressure of these with that of the contents of a plant cell whose protoplasmic sac contracts when the cell is introduced into a solution which has stronger attraction for water. By a systematic comparison of different solutions of the three substances named, with the same cells, three so-called isotonic liquids were obtained, *i. e.*, solutions of equal osmotic pressure. Then cells of another plant were used, and thus four such isotonic series were prepared, whereby a similar relation appeared in the respective concentrations, as

* *Osmotische Untersuchungen*, p. 71. [*This volume*, p. 10.]

† *Eine Methode zur Analyse der Turgorkraft*, Pringsheim's *Jahrb.*, **14**.

is shown in the following table, in which the concentration is expressed in gram-molecules* per litre:

Series	KNO_3	$C_{12}H_{22}O_{11}$	K_2SO_4	$KNO_3=1$	$C_{12}H_{22}O_{11}$	K_2SO_4
I.	0.12	—	0.09	1	—	0.75
II.	0.13	0.2	0.1	1	1.54	0.77
III.	0.195	0.3	0.15	1	1.54	0.77
IV.	0.26	0.4	—	1	1.54	—

Theoretical Demonstration.—Although the observations mentioned make it very probable that there is a proportionality between osmotic pressure and concentration, yet the theoretical demonstration is a welcome supplement, especially since it is almost self-evident. If we regard osmotic pressure as of kinetic origin, therefore as being produced by the impacts of the molecules of the dissolved substance, the demonstration depends upon the proportionality between the number of impacts in unit time and the number of molecules in unit space. The demonstration is, then, exactly the same as that for Boyle's law with ideal gases. If, on the other hand, we regard osmotic pressure as the expression of an attraction for water, the value of this is evidently proportional to the number of attracting molecules in unit volume, provided the dissolved molecules have no action upon one another, and each exerts, therefore, its own special attraction, as can be assumed with sufficiently dilute solutions.

3.—GAY-LUSSAC'S LAW FOR DILUTE SOLUTIONS.

While the proportionality between concentration and osmotic pressure at constant temperature is self-evident, it is different with the proportionality between osmotic pressure and absolute temperature at constant concentration. Nevertheless, this proposition can be demonstrated on thermodynamic grounds, and experimental data can also be cited which are very favorable to the results obtained thermodynamically.

Theoretical Demonstration.—It has already been mentioned that reversible transformations can be carried out by means of

* [*A gram-molecule of a substance is the molecular weight of the substance in grams, e.g. 58.5 grams of sodium chloride.*]

a piston and cylinder with semipermeable walls, which we will now use to complete a cycle. If we express this in the way which is well known for gases, volume and pressure are represented on the axes OV and OP, only that we must again deal here with the osmotic pressure. Let the original volume (VMr^3)* be represented by OA, the original pressure on the piston (PK^0), which is 1 Mr^2, by Aa, the absolute temperature by T; now let the solution undergo a minimum increase in volume of $dVMr^3$ ($=AB$) by moving the piston a distance $dVMr$, while the temperature of the solution is maintained constant by adding the requisite amount of heat. But this amount of heat can be determined at once, since it just serves to perform the known external work PdV, by moving the piston. No internal work is done, since we are dealing with a dilution which is so great that the dissolved molecules have no action upon one another. This isothermal change ab is followed by the so-called isentropic change bc, during which heat is neither given out nor absorbed. The temperature falls, then, dT, after which return to the original condition follows through a second isothermal and a second isentropic transformation, cd and da, respectively. As is known, the second law of thermodynamics requires that a fraction of the amount of heat PdV, imparted at the beginning, equal to $\frac{dT}{T}PdV$, is converted into work. This must, therefore, be equivalent to the area of the quadrilateral $abcd$; from which we obtain the following equation:

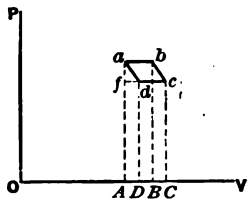

Fig. 3.

$$\frac{dT}{T}PdV = abcd = af.AB = afdV;$$

therefore:

$$P\frac{dT}{T} = af.$$

But af, in the above, is the change of the osmotic pressure at constant volume, resulting from a change in temperature dT, *i.e.*, $\left(\frac{dP}{dT}\right)_V dT$; from which, finally, we have:

* [*Mr is metre. K is kilogram.*]

$$\left(\frac{dP}{dT}\right)_v = \frac{P}{T}.$$

This equation gives, however, on integration, keeping volume constant:

$$\frac{P}{T} = \text{constant}.$$

That is to say, the osmotic pressure is proportional to the absolute temperature, in case volume or concentration remains the same, which proposition for solutions is perfectly analogous to the law of Gay-Lussac for gases.

Experimental Proof. Determination of the Osmotic Pressure at Different Temperatures.—Let us next compare the theoretical conclusion just reached with the results of Pfeffer's investigations.* This investigator found, as a matter of fact, that the osmotic pressure, without exception, increases with rise in temperature. We will, moreover, see that although the experimental results referred to do not suffice to make the above proposition absolutely certain, yet an excellent approximation between observation and calculation often appears. If from one of two experiments carried out with the same solution at different temperatures we calculate the result of the other, on the assumption of Gay-Lussac's law, and compare it with the value directly obtained, we have:

1. Solution of cane-sugar.
   At 32° a pressure of 544 millimetres was observed.
   At 14°.15 the calculated pressure is 512 millimetres, instead of 510 millimetres observed.
2. Solution of cane-sugar.
   At 36° the pressure observed was 567 millimetres.
   At 15°.5 the calculated pressure is 529 millimetres, instead of 520.5 millimetres observed.
3. Solution of sodium tartrate.
   At 36°.6 the pressure observed was 1564 millimetres.
   At 13°.3 the calculated pressure is 1443 millimetres, instead of 1431.6 millimetres found.
4. Solution of sodium tartrate.
   At 37°.3 the pressure observed was 983 millimetres.
   At 13°.3 the calculated pressure is 907 millimetres, instead of 908 millimetres found.

* *Osmotische Untersuchungen*, pp. 114, 115. [*This volume*, p. 10.]

Experimental Proof. Comparison of Osmotic Pressure by Physiological Methods.—Just as the law of Boyle, applied to solutions, received support from the fact that isotonic solutions of different substances preserve equality of osmotic pressure when the respective concentrations were reduced to the same fraction, so the law of Gay-Lussac is supported by the result that this isotonism is likewise preserved for equal change in temperature. This fact was also established by physiological methods, this time by Donders and Hamburger,* who, working in a manner similar to that of De Vries, but now with animal cells (blood corpuscles), found that solutions of potassium nitrate, sodium chloride, and sugar, which are isotonic with the contents of the cells in question, at 0°, and, therefore, with one another, show exactly the same relation at 34°, as will be seen from the following table:

	TEMPERATURE 0°.	TEMPERATURE 34°.
KNO_3	1.052–1.03 %	1.052–1.03 %
Na Cl	0.62 –0.609 %	0.62 –0.609 %
$C_{12}H_{22}O_{11}$	5.48 –5.38 %	5.48 –5.38 %

Experimental Proof of the Laws of Boyle and Gay-Lussac for Solutions. Experiments of Soret.†—The phenomenon observed by Soret is very significant for the analogy between gases and solutions, where we are dealing with the influence of concentration and temperature on the pressure and on osmotic pressure respectively. It became apparent from these experiments that, just as with a difference in temperature in gases, the warmest part is the most dilute, so, also, with solutions the same relation obtains; only that in the latter case the time required to establish the final condition of equilibrium is considerably greater. The experiments were made in vertical tubes, in such a manner that the upper portion of the solution contained in them, which was perfectly homogeneous at the beginning, was warmed at a constant temperature, while the under portion was likewise cooled to a definite temperature.

* *Onderzoekingen gedaan in het physiologisch. Laboratorium der Utrechtsche Hoogeschool*, (3), **9**, 26.

† *Archives des Sciences phys. et nat.*, (3), **2**, 48; *Ann. Chim. Phys.*, (5), **22**, 293.

If, then, the observation of Soret contains, qualitatively, a complete confirmation of the laws developed, so, also, a welcome approximation to our theory is to be found in his quantitative results, at least in the latest experiments. It would be expected, as with gases, that equilibrium exists when the isotonic state is reached; and where the osmotic pressure increases proportional to the concentration and to the absolute temperature, this isotonic state of the parts of the solution will occur when the products of the two values are equal.

If, on this basis, we calculate the concentration of the warmer part of the solution from that which was found in the colder part, and compare with this the value obtained directly by experiment, we have:

1. Solution of copper sulphate.
   The part cooled to 20° contained 17.332 per cent. 14.3 per cent. would correspond to a temperature of 80°; instead of this, 14.03 per cent. was found.
2. Solution of copper sulphate.
   The part cooled to 20° contained 29.867 per cent. 24.8 per cent. would correspond to a temperature of 80°; instead of this, 23.871 per cent. was found.

It must, indeed, be added that the earlier experiments of Soret gave less favorable results, yet, on account of the difficulty of such observations, too much stress must not be laid upon them.

4.—AVOGADRO'S LAW FOR DILUTE SOLUTIONS.

While up to the present essentially only those changes have been dealt with which the osmotic pressure in solutions undergoes due to changes in concentration and temperature, and while the agreement with the corresponding laws which hold for gases manifested itself, we must now deal with the direct comparison of the two analogous quantities, elastic pressure and osmotic pressure of one and the same substance. It is evident that this applies to gases which have also been investigated in solution; and, as a matter of fact, it will be proved that, in case the law of Henry is satisfied, the osmotic pressure in solution is exactly equal to the elastic pressure as gas, at least at the same temperature and concentration.

For the purpose of demonstration, we will perform a reversible cycle at constant temperature, by means of semipermeable walls, and then employ the second law of thermodynamics, which, in this case, as is known, leads to an extremely simple result, that no heat is transformed into work, or work into heat, and consequently the sum of all the work done must be equal to zero.

The reversible cycle is performed by two similarly arranged double cylinders, with pistons, like one already described. One cylinder is partly filled with a gas (A), say oxygen, in contact with a solution of oxygen (B), saturated under the conditions of the experiment; for example, an aqueous solution. The wall bc allows only oxygen but no water to pass through; the wall ab, on the contrary, allows water but not oxygen to pass, and is in contact on the outside with the liquid (E) in question. A reversible transformation can be made with such a cylinder; which amounts to this, that by raising the two pistons (1) and (2) oxygen is evolved from its aqueous solution as gas, while water is removed through ab. This transformation can take place so that the concentrations of gas and solution remain the same. The only difference between the two cylinders is in the concentrations which are present in them. These we will express in the following manner:

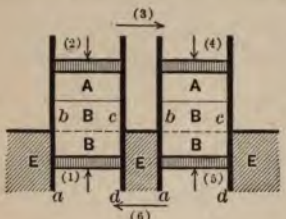

Fig. 4

The unit of weight of the substance in question fills, in the left vessel, as gas and as solution, the volumes v and V respectively, in the right of $v+dv$ and $V+dV$; then, in order that Henry's law be satisfied, the following relation must obtain:

$$v : V = (v+dv) : (V+dV)$$

therefore:

$$v : V = dv : dV.$$

Let now the pressure and osmotic pressure of gas and solution, in case unit weight is present in unit volume, be respectively P and p (values which hereafter will be shown to be equal), the pressure in gas and solution is, then, from Boyle's law, respectively, $\frac{P}{v}$ and $\frac{p}{V}$.

If we now raise the pistons (1) and (2), and thus liberate a unit weight of the gas from the solution, we increase, then,

this gas volume v by dv, in order that it may have the concentration of the gas in the left vessel; if the gas just set free is forced into solution by lowering pistons (4) and (5), and thus the volume of the solution $V+dV$ diminished by dV in the cylinder with semipermeable walls, the cycle is then completed.

Six amounts of work are to be taken into consideration, whose sum, from what is stated above, must be equal to zero. We will designate these by numbers, whose meaning is self-evident. We have, then:

$$(1)+(2)+(3)+(4)+(5)+(6)=0.$$

But (2) and (4) are of equal value and opposite sign, since we are dealing with volume changes v and $v+dv$, in the opposite sense, which take place at pressures which are inversely proportional to the volumes. For the same reasons the sum of (1) and (5) is zero; then, from the above relation:

$$(3)+(6)=0.$$

The work done by the gas (3), in case it undergoes an increase in volume dv at a pressure $\frac{P}{v}$, is:

$$(3)=\frac{P}{v}dv,$$

while the work done by the solution (6), in case it undergoes a diminution in volume dV at an osmotic pressure $\frac{p}{V}$, is:

$$(6)=-\frac{p}{V}dV.$$

We obtain, then:

$$\frac{P}{v}dv=\frac{p}{V}dV;$$

and since $v:V=dv:dV$, P and p must be equal, which was to be proved.

The conclusion here reached, which will be repeatedly confirmed in what follows, is, in turn, a new support to the law of Gay-Lussac applied to solutions. In case gaseous pressure and osmotic pressure are equal at the same temperature, changes in temperature must have also an equal influence on both. But, on the other hand, the relation found permits of an important extension of the law of Avogadro, which now finds application also to all solutions, if only osmotic pressure is considered instead of elastic pressure. At equal osmotic pressure and equal temperature, equal volumes of the most

widely different solutions contain an equal number of molecules, and, indeed, the same number which, at the same pressure and temperature, is contained in an equal volume of a gas.

5.—GENERAL EXPRESSION OF THE LAWS OF BOYLE, GAY-LUSSAC, AND AVOGADRO, FOR SOLUTIONS AND GASES.

The well-known formula, which expresses for gases the two laws of Boyle and Gay-Lussac:

$$PV = RT,$$

is now, where the laws referred to are also applicable to liquids, valid also for solutions, if we are dealing with the osmotic pressure. This holds even with the same limitation which is also to be considered with gases, that the dilution shall be sufficiently great to allow one to disregard the reciprocal action of, and the space taken by, the dissolved particles.

If we wish to include in the above expression, also, the third, the law of Avogadro, this can be done in an exceedingly simple manner, following the suggestion of Horstmann,* considering always kilogram-molecules of the substance in question; thus, 2 k. hydrogen, 44 k. carbon dioxide, etc. Then R in the above equation has the same value for all gases, since at the same temperature and pressure the quantities mentioned occupy also the same volume. If this value is calculated, and the volume taken in Mr^3, the pressure in K^0 per Mr^2, and if, for example, hydrogen at 0° and atmospheric pressure is chosen:

$$P = 10333,\ V = \frac{2}{0.08956},\ T = 273,\ R = 845.05.$$

The combined expression of the laws of Boyle, Gay-Lussac, and Avogadro is, then:

$$PV = 845\ T,$$

and in this form it refers not only to gases, but to all solutions, P being then always taken as osmotic pressure.

In order that the formula last obtained may be hereafter easily applied, we give it finally a simpler form, by observing that the number of calories, which is equal to a kilogram-metre, therefore to the equivalent of work† $\left(A = \frac{1}{423}\right)$, stands in a very

* *Ber. deutsch. chem. Gesell.*, **14**, 1243.

† [*The reciprocal of the "mechanical equivalent of heat."*]

simple relation to R, indeed, $AR=2$ (more exactly, about one-thousandth less).

Therefore, the following form can be chosen :

$$APV=2\,T,$$

which has the great practical advantage that the work done, of which we shall often speak hereafter, finds a very simple expression, in case it is calculated in calories.

Let us next calculate the work, expressed in calories, which is done when a gas or a solution at constant pressure and temperature expands by a volume V, a kilogram-molecule being the mass involved. This work is evidently $2\,T$. We should add that this constant pressure is preserved only if the entire volume of gas or solution is very large in proportion to V, or if we are dealing with vaporization at maximum tension.

The subordinate question will often arise, of the work expressed in calories, which is done by isothermal expansion, either by a kilogram-molecule of a gas, or, if it is a solution, by that amount which contains this quantity of the dissolved substance. If the pressure decreases, then, by a very small fraction ΔP, which therefore corresponds to an increase in volume of ΔV, the work done will be $AP\Delta V$, or $2\,\Delta T$.

6.—FIRST CONFIRMATION OF AVOGADRO'S LAW AS APPLIED TO SOLUTIONS. DIRECT DETERMINATION OF OSMOTIC PRESSURE.

It would be expected beforehand that the law of Avogadro, which we developed for solutions of gases, as a consequence of the law of Henry, would not be limited to solutions of those substances which, perchance, are in the gaseous state under ordinary conditions. Yet the confirmation of this conjecture is very welcome in other cases, especially in those now to be mentioned, since we are not dealing here with theoretical conclusions, but with the results of direct experiment. As a matter of fact, we will find in Pfeffer's determinations of the osmotic pressure of solutions of sugar* a striking confirmation of the law which we are defending.

A one-per-cent. solution of sugar was used in the experiment under consideration, *i. e.*, a solution obtained by bringing

* *Osmotische Untersuchungen*, Leipsic, 1877.

together 1 part of sugar and 100 parts of water, which contained, then, 1 gram of the substance named, in 100.6 cm.³ of the solution. If we compare the osmotic pressure of this solution with the pressure of a gas—say hydrogen—which contains the same number of molecules in 100.6 cm.³, therefore, in the case chosen, $\frac{2}{342}$ grams ($C_{12}H_{22}O_{11}=342$), a striking agreement becomes manifest. Since hydrogen at one atmosphere pressure and at 0° weighs 0.08956 grams per litre, and the above concentration contains 0.0581 grams per litre, we are dealing at 0°, with 0.649 atmosphere, and, therefore, at $t°$, with $0.649\,(1+0.00367\,t)$. If we compare these with Pfeffer's data, we have:

TEMPERATURE (t).	OSMOTIC PRESSURE.	$0.649\,(1+0.00367\,t)$.
6.8	0.664	0.665
13.7	0.691	0.681
14.2	0.671	0.682
15.5	0.684	0.686
22.0	0.721	0.701
32.0	0.716	0.725
36.0	0.746	0.735

The osmotic pressure of a solution of sugar, ascertained directly, is, then, at the same temperature, exactly equal to the gas pressure of a gas which contains the same number of molecules in a given volume as there are sugar molecules in the same volume of the solution.

This relation can be extended from cane-sugar to other dissolved substances; as invert sugar, malic acid, tartaric acid, citric acid, malate and sulphate of magnesium, which, from the physiological investigations* of De Vries, show the same osmotic pressure for equal molecular concentration of the solutions.

7.—SECOND CONFIRMATION OF THE LAW OF AVOGADRO AS APPLIED TO SOLUTIONS. MOLECULAR LOWERING OF VAPOR-PRESSURE.

The relation which exists between osmotic pressure and maximum vapor-tension, and which can be easily developed on

* *Eine Methode zur Messung der Turgorkraft*, 512.

thermodynamic grounds, furnishes a suitable means of testing the laws in question, through the experimental material recently collected by Raoult.

We shall then begin with a perfectly general law, which is entirely independent of that hitherto developed: *Isotonism in solutions in the same solvent conditions equality of maximum tension.* This proposition can be easily demonstrated by carrying out a reversible cycle at constant temperature. For this purpose two solutions are taken with the same maximum tension, and a small amount of the solvent is transported, in a reversible manner, from one to the other, as vapor, *i. e.*, with piston and cylinder. This transference takes place when the maximum tensions are equal, without doing work, therefore no work is done in returning the solvent, since in the whole cycle no work can be done. If we now return the solvent by means of a semipermeable wall, which separates the two solutions, the necessity of the isotonic state is at once evident, since otherwise this transformation could not take place without doing work.

If we apply this principle to dilute solutions, with the aid of the laws developed for them, we arrive at once at the simple conclusion that equal molecular concentration of dissolved substance conditions equal maximum tension of the solution. But this is exactly the principle recently discovered by Raoult,* of the constancy of molecular lowering of vapor-pressure. This is, however, obtained by multiplying the molecular weight of dissolved substances with the so-called relative lowering of the vapor-pressure of a one-per-cent. solution, *i. e.*, with the part of the maximum tension which the solvent has thus lost. The equality of the molecular lowering of vapor-pressure refers then to solutions of equi-molecular concentration, on the assumption of the approximate proportionality between lowering of vapor-pressure and concentration. For example, the value in question for ether, for the thirteen substances which were investigated in it, fluctuated between 0.67 and 0.74, with a mean of 0.71.

But we can carry this relation still further, and compare the different solvents with one another, to arrive at the second law which Raoult likewise found experimentally. For this purpose, we perform, at $T°$, with a very dilute

* *Comp. rend.*, **87**, 167; **44**, 1431.

P-per-cent. solution, the following reversible cycle, consisting of two parts:

1. That mass of the solvent is removed by means of piston and cylinder in which a kilogram-molecule (M) of the dissolved substance is contained. The mass of the solution is so large that change in concentration is not thus produced, and the work done amounts, therefore, to $2\,T$.

2. The amount of solvent just obtained, $\frac{100\,M}{P}$ kilograms, is returned as vapor in a reversible way, therefore first obtained from the liquid at maximum tension, then expanded until the maximum tension of the solution is reached, and finally liquefied in contact with the solution. The kilogram-molecule of the solvent (M') would require, thus, an expenditure of $2\,\Delta T$ work, in which Δ represents the relative lowering of vapor-pressure; and therefore the $\frac{100\,M}{P}$ kilograms in question would require $2\,T\Delta\frac{100\,M}{PM'}$. But $\frac{\Delta}{P}M$ is Raoult's molecular lowering of vapor-pressure, which we will therefore represent by the letter K, whence the expression in question becomes simplified to $\frac{200\,TK}{M'}$.

But from the second law of thermodynamics, the sum of the work done in this cycle, completed at constant temperature, must again be equal to zero, therefore what is gained in the first part is expended in the second. We have, consequently:

$$2\,T=\frac{200\,TK}{M'} \text{ or } 100\,K=M'.$$

This relation comprises all of Raoult's results. It expresses, at once, what was obtained above, that the molecular lowering of the vapor-pressure is independent of the nature of the dissolved substance. But it shows, also, what Raoult found, that the value in question does not change with the temperature. It contains, finally, the second proposition of Raoult, that the molecular lowering of the vapor-pressure is proportional to the molecular weight of the solvent, and amounts to about one one-hundredth of it. The following figures, obtained by Raoult, suffice to show this:

SOLVENT.	MOLECULAR WEIGHT (M').	MOLECULAR LOWERING OF VAPOR-PRESSURE (K).
Water	18	0.185
Phosphorus trichloride	137.5	1.49
Carbon bisulphide	76	0.80
Carbon tetrachloride	154	1.62
Chloroform	119.5	1.30
Amylene	70	0.74
Benzene	78	0.83
Methyl iodide	142	1.49
Methyl bromide	109	1.18
Ether	74	0.71
Acetone	58	0.59
Methyl alcohol	32	0.33

8.—THIRD CONFIRMATION OF AVOGADRO'S LAW AS APPLIED TO SOLUTIONS. MOLECULAR LOWERING OF THE FREEZING-POINT.

There can also be stated here a perfectly general and rigid proposition, which connects the osmotic pressure of a solution with its freezing-point. *Solutions in the same solvent, having the same freezing-point, are isotonic at that temperature.* This proposition can be proved exactly as the preceding one, by carrying out a cycle at the freezing-point of the two solutions; only here the reversible transference of the solvent is effected not as vapor, but as ice. It is returned again through a semi-permeable wall, and since there can be no work done, isotonism must exist.

We also apply this proposition to dilute solutions, and if we take into account, then, the relations already developed, we arrive at once at the very simple conclusion that solutions which contain the same number of molecules in the same volume, and, therefore, from Avogadro's law, are isotonic, have also the same freezing-point. This was, in fact, discovered by Raoult, and found its expression in the term introduced by him, the so-called "normal molecular lowering of the freezing-point," which is shown by the large majority of dissolved substances, and means that the freezing-point lowering of a one-per-cent. solution, multiplied by the molecular weight, is constant. This refers, therefore, to solutions of equal molecular concentration,

on the assumption of an approximate proportionality between concentration and lowering of freezing-point. For example, this value is about 18.5 for almost all organic substances dissolved in water.

We can, however, carry the relation still further, and derive the above normal molecular lowering of the freezing-point from other data, on the assumption of Avogadro's law for solutions. This quantity bears a necessary and simple relation to the latent heat of fusion of the solvent, as the following reversible cycle shows, using the second law of thermodynamics. Let us take a very dilute P-per-cent. solution, which gives a freezing-point lowering Δ; the solvent freezes at T, and its latent heat of fusion is W per kilogram.

1. The solution is deprived at T, of that amount of the solvent in which a kilogram-molecule (M) of the dissolved substance is present, exactly as in the preceding case, by means of piston and cylinder with semipermeable wall. The amount of the solution is here so large that change in concentration is not thus produced, and therefore the work done is $2\,T$.

2. The $\frac{100\,M}{P}$ kilograms of the solvent obtained, is allowed to freeze at T, when $\frac{100\,MW}{P}$ calories are set free. The solution and solid solvent are cooled Δ degrees, and the latter allowed to melt in contact with the solution, thereby taking up the heat just set free. Finally, the temperature is again raised Δ degrees.

In this reversible cycle $\frac{100\,MW}{P}$ calories are raised from $T-\Delta$ to T, which corresponds to an amount of work $\frac{100\,MW\Delta}{PT}$, but $\frac{M\Delta}{P}$ is the molecular lowering of the freezing-point, which we will designate by the letter t; the work done is, therefore, $\frac{100\,Wt}{T}$, and this was shown in the first part of the above process to be $2\,T$; therefore:

$$\frac{100\,Wt}{T}=2\,T,$$

or

$$t=0.02\,\frac{T^2}{W}.$$

The relation thus obtained is very satisfactorily confirmed by the facts. We give the values calculated from the formula developed, together with the molecular freezing-point lowerings obtained by Raoult,* so that the two may be examined.

SOLVENT.	FREEZING-POINT (T).	LATENT HEAT OF FUSION (W).	$t=\frac{0.02\,T^2}{W}$.	MOLECULAR LOWERING.
Water.....	273	79	18.9	18.5
Acetic acid...	273+16.7	43.2†‡	38.8	38.6
Formic acid..	273+ 8.5	55.6†‡	28.4	27.7
Benzene.....	273+ 4.9	29.1‡	53.0	50.0
Nitrobenzene.	273+ 5.3	22.3‡	69.5	70.7

Let us add, that from the lowering found for ethylene bromide, 117.9, the latent heat of fusion of this substance, unknown at that time, was calculated to be 13, and that the determination which Pettersson very kindly carried out at my request gave, in fact, the value expected (mean, 12.94).

9. — APPLICATION OF AVOGADRO'S LAW TO SOLUTIONS. GULDBERG AND WAAGE'S LAW.

Having given the physical side of the problem the greater prominence, thus far, in order to furnish the greatest possible support to the principles developed, it now remains to apply it to chemistry. The most obvious application of the law of Avogadro for solutions, as for gases, is to ascertain the molecular weight of dissolved substances. This application has, indeed, already been made, only it consists not in the investigation of pressures as with gases, where every determination of molecular weight amounts to the determination of pressure, volume, temperature, and weight. In solutions we would have to deal in such an experimental arrangement, with the determination of the osmotic pressure, and the practical means of determining this are still wanting. Yet this obstacle can be overcome by determining, instead of the osmotic pressure, one of the two values which, from what is given above, are connected with it, *i. e.*, the diminution of vapor-pressure or the lowering of the freezing-point. To this end there is the proposition

* *Ann. Chim. Phys.*, (5), **28**, (6), **11**.
† Berthelot, *Essai de Mécanique Chimique.*
‡ Pettersson, *Journ. prakt. Chim*, (2), **24**, 129.

of Raoult already made use of for determining molecular weights — *viz.*, the relative lowering of vapor-pressure of a one-per-cent. aqueous solution is to be divided into 0.185, or the freezing-point lowering is to be divided into 18.5, a method which is comparable with those used for such determinations with gases, and the results of which, therefore, confirm Avogadro's law for solutions.

It is still more remarkable that the so general law of Guldberg and Waage, assumed also for solutions, can, in fact, be developed as a simple conclusion from the laws adduced above for dilute solutions. It is only necessary to complete a reversible cycle at constant temperature, which can be done with semi-permeable walls, as well with solutions as with gases.

Let us imagine two systems of gaseous or dissolved substances in equilibrium, and let us represent this condition, in general, by the following symbol:

$$a_1'M_1' + a_1''M_1'' + \text{etc.} \gtrless a_{11}'M_{11}' + a_{11}''M_{11}'' + \text{etc.},$$

in which a represents the number of molecules, and M the [*chemical*] formula. This equilibrium exists in two vessels, A and B, at the same temperature, but at different concentrations. We will designate the latter by the partial pressure, or the osmotic pressure which each of the substances in question exercises. Let these pressures in vessel A be, $P_1'P_1''..P_{11}'P_{11}''$, etc.: in B they are larger by $dP_1'dP_1''...dP_{11}'dP_{11}''$, etc.

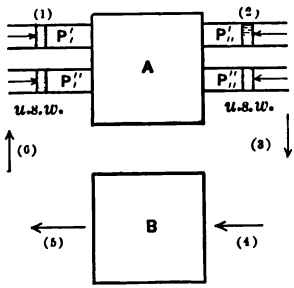

Fig. 5

The reversible cycle, to be carried out, consists in this: the mass of the first system, expressed by the above symbol, is introduced into A in kilograms, while the second is removed in equivalent quantity. Both have here the concentrations which exist in A. This transformation is so carried out that every one of the substances in question enters or leaves by means of a suitable piston and cylinder, which is separated from the vessel A by a wall, permeable to this substance alone. If we are dealing with a solution, the cylinders themselves are made with a semi-permeable wall, and are surrounded with the solvent.

If this is accomplished, every part of the second system

undergoes the change in concentration necessary to become equal to that which exists in B. The work done, per kilogram-molecule, is, as before, $2\Delta T$; in which Δ is the fraction of the increase in pressure, therefore here $\frac{dP}{P}$; for the amounts in question the work done is then $2aT\frac{dP}{P}$.

The second system just obtained, is now conducted over into the first by means of the vessel B, exactly as above, at the concentrations prevailing in B, and these are finally changed into the original concentrations existing in A, by suitable change in volume.

Where we are dealing with a cycle completed at constant temperature the sum of the amounts of work in question is zero, and this can be indicated by the following equation, which, indeed, needs no explanation:

$$(1)+(2)+(3)+(4)+(5)+(6)=0.$$

If we observe that (1) and (5) are transformations, in the reverse sense, of the same parts, with the same mass, at the same temperature, it follows that:

$$(1)+(5)=0;$$

and, for the same reasons:

$$(2)+(4)=0;$$

from which we conclude that:

$$(3)+(6)=0.$$

But this leads immediately to the law of Guldberg and Waage.

The amount of work (3) is, indeed, from the foregoing, $\Sigma 2a_{,,} T\frac{dP_{,,}}{P_{,,}}$, and likewise (6) is equal to $\Sigma 2a_{,} T\frac{dP_{,}}{P_{,}}$, whence it follows:

$$\Sigma\left(2a_{,,} T\frac{dP_{,,}}{P_{,,}}-2a_{,} T\frac{dP_{,}}{P_{,}}\right)=0,$$

or:

$$\Sigma\left(a_{,,}\frac{dP_{,,}}{P_{,,}}-a_{,}\frac{dP_{,}}{P_{,}}\right)=0.$$

On integration we obtain:

$$\Sigma\,(a_{,,}\log P_{,,}-a_{,}\log P_{,})=\text{constant},$$

but in this P is proportional to the concentration or active mass C, and the latter can therefore be introduced instead of the former without destroying the constancy of the whole expression. Therefore:

$$\Sigma\,(a_{,,}\log C_{,,}-a_{,}\log C_{,})=\text{constant},$$

which is nothing but the Guldberg-Waage formula in logarithmic form.

10.—DEVIATIONS FROM AVOGADRO'S LAW IN SOLUTIONS. VARIATION FROM THE GULDBERG-WAAGE LAW.

We have tried to show in the preceding portion of this paper, the genetic connection which exists between the Guldberg-Waage law and the known or newly established laws for solutions of Boyle, Henry, Gay-Lussac, and Avogadro. It is the same which, indeed, long ago, allowed the law of Guldberg and Waage to be demonstrated for gases on thermodynamic grounds.

It is now a question of further developing the laws of chemical equilibrium, and, therefore, at first, we must examine more closely the real validity of the three principles from which the law of Guldberg and Waage is derived.

If we are still considering "ideal solutions," a class of phenomena must be dealt with which, from the now clearly demonstrated analogy between solutions and gases, are to be classed with the earlier so-called deviations of gases from Avogadro's law. As the pressure of the vapor of ammonium chloride, for example, was too great in terms of this law, so, also, in a large number of cases the osmotic pressure is abnormally large; and as was afterwards shown, in the first case there is a breaking down into hydrochloric acid and ammonia, so also with solutions we would naturally conjecture that, in such cases, a similar decomposition had taken place. Yet it must be conceded that anomalies of this kind, existing in solutions, are much more numerous, and appear with substances which, it is difficult to assume, break down in the usual way. Examples in aqueous solutions are most of the salts, the strong acids, and the strong bases; and, therefore, the existence of the so-called normal molecular lowering of the freezing-point and diminution of the vapor-pressure were not discovered until Raoult employed the organic compounds. These substances, almost without exception, behave normally. It may, then, have appeared daring to give Avogadro's law for solutions such a prominent place, and I should not have done so had not Arrhenius pointed out to me, by letter, the probability that salts and analogous substances, when in solution, break down into ions. As a matter of fact, as far as investigation has

been carried, the solutions which obey the law of Avogadro are non-conductors, which indicates that they are not broken down into ions; and a further experimental examination of the other solutions is possible, since, from the assumption made by Arrhenius, the deviation from Avogadro's law can be calculated from the conductivity.

However this may be, the attempt will now be made to take into account these so-called deviations from Avogadro's law, and, retaining the laws of Boyle and Gay-Lussac for solutions, to give the development, thus made possible, of Guldberg and Waage's formula. The change which the expressions hitherto developed undergo, can be made easily and briefly when what is stated above is taken into account.

The combined expression of the laws of Boyle, Gay-Lussac, and Avogadro developed on page 25:

$$APV = 2T,$$

is changed into:

$$APV = 2iT,$$

where the pressure is in general i times the value presupposed in the above expression.

Therefore, the work done by reversible change in solutions will be i times the former value, and this sums up the entire transformation to be introduced, which is then easily applied to the development of the Guldberg and Waage formula just given.

If we return to the relation obtained at the end of the completed cycle, page 33:

$$(3)+(6)=0,$$

the amounts of work done, (3) and (6), which were formerly represented by $\Sigma 2a_{,,} T\frac{dP_{,,}}{P_{,,}}$ and $-\Sigma 2a_{,} T\frac{dP_{,}}{P_{,}}$, are now expressed by i times these respective values. The result is consequently:

$$\Sigma\left(a_{,,}i_{,,}\frac{dP_{,,}}{P_{,,}} - a_{,}i_{,}\frac{dP_{,}}{P_{,}}\right)=0.$$

After integration we have:

$$\Sigma\left(a_{,,}i_{,,}\log P_{,,} - a_{,}i_{,}\log P_{,}\right)=\text{constant},$$

and by introducing the concentration or active mass C, instead of the pressure which is proportional to it:

$$\Sigma\left(a_{,,}i_{,,}\log C_{,,} - a_{,}i_{,}\log C_{,}\right)=\text{constant}.$$

This is, then, the logarithmic statement of the Guldberg-Waage formula in its new form, which differs from the earlier

form only in that it contains the quantity i. It now remains to show that the newly obtained relation agrees very much better with the facts than the original expression. It is, therefore, necessary to know exactly the values of i, in question, and in this we are limited to aqueous solutions, since only here is there sufficient experimental data at hand to make the examination desired.

11.—DETERMINATION OF i FOR AQUEOUS SOLUTIONS.

Since we have succeeded in establishing Avogadro's law for solutions in four different ways, there are also four ways of studying the deviations referred to, therefore of determining i. But of these, that which depends upon the lowering of the freezing-point so far surpasses the others, due to the extended and careful investigations in this field, that we can limit ourselves entirely to this method.

Let us then return to the cycle which, on the basis of freezing-point determinations, led us to Avogadro's law. This gave the relation:

$$\frac{100\,Wt}{T}=2\,T,$$

in which the second term represents the work done by reversibly removing that amount of the solvent which contains a kilogram-molecule dissolved in it. This must then be multiplied by i:

$$\frac{100\,Wt}{T}=2\,iT.$$

From this there appears at once a very simple way of determining i. This value, from the above equation, seems to be proportional to t, *i. e.*, to the molecular lowering of the freezing-point, since all other values (T, absolute temperature of fusion—W, latent heat of fusion of solvent) are constant. But 18.5 is the molecular lowering of the freezing-point for cane-sugar, which, from page 25, rigidly obeys the law of Avogadro, and for which, therefore, $i=1$. The value of i for other substances is, therefore, the lowering produced by them, divided by 18.5. Almost exactly the same result is obtained if, in the above equation, for T and W the corresponding values for ice, 273 and 79, respectively, are introduced. They will, therefore, be used in the following calculations.

12.—PROOF OF THE MODIFIED GULDBERG-WAAGE LAW.

In using the relation now proposed, and in the comparison with the results of the Guldberg-Waage formula to be made by the reader, it is necessary to mention briefly the different forms which the latter has taken in the course of time. We will first represent our relation by a simple formula, in which also Guldberg and Waage's conceptions can be expressed, *viz.*:

$$\Sigma ai \log C = K. \qquad (1)$$

It differs from the expression on page 35 only in this, the terms referring to the constituent parts of the two systems are regarded with inverse signs. The original expression of the Swedish* investigators† is, then, very similar to the above:

$$\Sigma k \log C = K, \qquad (2)$$

only that here k is to be determined for each constituent in question by observing the equilibrium of the system.

But when Guldberg and Waage repeatedly found the coefficient in question k, to be equal to 1, in the observations‡ which they had made bearing upon this point, they gave their law the simplified form:

$$\Sigma \log C = K. \qquad (3)$$

In their last communication,§ however, the change is introduced which takes into account also the number of molecules a, and therefore the following relation obtains, corresponding to the formula since developed for gases on thermodynamic grounds:

$$\Sigma a \log C = K. \qquad (4)$$

We have, therefore, designated this above as the Guldberg-Waage formula.

Although this simplified expression, with coefficients which are whole numbers, was defended for solutions by the Swedish Investigators, Lemoine,‖ on the basis of Schloesing's experiments on the solubility of calcium carbonate in water containing carbon dioxide, returned, not long ago, to the original

* [*Guldberg and Waage are Professors in the University of Christiania.*]
† *Christiania Videnskabs Selskabs Forhandlingar*, 1864.
‡ *Études sur les affinités chimiques*, 1867.
§ *Journ. prakt. Chem.*, **19**, 69.
‖ *Études sur les équilibres chimiques*, 266.

formula (2), with coefficients which remain to be more accurately determined, but which were, in general, not whole numbers; and, indeed, if whole numbers were employed, there was not an agreement between fact and theory.

In view of this uncertainty, the formula which we have introduced has the advantage that the coefficients which appear in it are completely determined at the outset, and therefore their correctness can be decided at once by experiment. It will, in fact, become apparent that in the cases studied by Guldberg and Waage, through the peculiar values of i, the simple form brought forward by these investigators as of general applicability, is completely verified, and the fact that such simplification is in most cases permissible is in accordance with what we have laid stress upon above—*viz.*, the validity of Avogadro's law for solutions. On the other hand, the investigation of Schloesing, brought prominently forward by Lemoine, would show that the simplification in question is not allowable, since with it the same fractional coefficients appeared which Schloesing obtained.

Before we can proceed to examine our relation more closely, it is necessary to adapt it also to the case where, in part, undissolved substances are present. This is very simply done, and leads to the same result for all of the above-mentioned formulas; if we consider that such substances are present in the solution, even to saturation, therefore at constant concentration. All such concentrations can then be transferred from the first term of the above equation to the second, without destroying the constancy of the latter. All remains, then, exactly the same, only that the dissolved substances are to be considered exclusively in the first term.

1. We will first examine the observations of Guldberg and Waage. These investigators studied chiefly the equilibrium expressed by the following symbol:

$$Ba\,CO_3 + K_2\,SO_4 \rightleftarrows Ba\,SO_4 + K_2\,CO_3,$$

and found, corresponding to their simplified formula:

$$\log C_{K_2SO_4} - \log C_{K_2CO_3} = K.$$

But from our equation almost exactly the same relation results, since for $K_2\,SO_4$, $a=1$ and $i=2.11$; for $K_2\,CO_3$, $a=1$ and $i=2.26$; therefore:

$$\log C_{K_2SO_4} - 1.07 \log C_{K_2CO_3} = K.$$

The same agreement exists between the two results, in case we

are dealing with the sodium salts, since where i for Na_2SO_4 and Na_2CO_3 is 1.91 and 2.18 respectively, we obtain the following relation:

$$\log C_{Na_2SO_4} - 1.14 \log C_{Na_2CO_3} = K.$$

2. But in the above-mentioned experiments of Schloesing* we do not expect these nearly integral numbers. It was a question there of the solubility of calcium carbonate in water containing carbon dioxide, therefore of an equilibrium which can be expressed by the following symbol:

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2.$$

We expect, then, since $i=1$ for carbon dioxide, and $i=2.56$ for acid calcium carbonate:

$$0.39 \log C_{H_2CO_3} - \log C_{Ca(HCO_3)_2} = K,$$

while Schloesing found the following relation:

$$0.37866 \log C_{H_2CO_3} - \log C_{Ca(HCO_3)_2} = K.$$

The agreement is also very satisfactory for the corresponding phenomenon with barium, since i for acid barium carbonate being 2.66, we obtain:

$$0.376 \log C_{H_2CO_3} - \log C_{Ba(HCO_3)_2} = K,$$

while experiment gave:

$$0.38045 \log C_{H_2CO_3} - \log C_{Ba(HCO_3)_2} = K.$$

3. Let us now turn to Thomsen's experiments† on the action of sulphuric acid on sodium nitrate in solution. This investigator arrived at the result that the state of the case as foreseen by Guldberg and Waage actually obtains. But this is, indeed, another one of the cases where our relation and Guldberg-Waage's formula lead to the same result.

If we express the equilibrium in question by the following symbol:

$$Na_2SO_4 + HNO_3 \rightleftarrows NaHSO_4 + NaNO_3,$$

Guldberg-Waage's relation requires:

$$\log C_{Na_2SO_4} + \log C_{HNO_3} - \log C_{NaHSO_4} - \log C_{NaNO_3} = K.$$

But:

$$i_{Na_2SO_4} = 1.91,\ i_{HNO_3} = 1.94,\ i_{NaHSO_4} = 1.88,\ i_{NaNO_3} = 1.82,$$

and we obtain then:

$$1.05 \log C_{Na_2SO_4} + 1.06 \log C_{HNO_3} - 1.03 \log C_{NaHSO_4} - \log C_{NaNO_3} = K,$$

which amounts to almost the same thing.

* *Compt. rend.*, **74**, 1552; **75**, 70.

† *Thermochemisch Untersuchungen*, **1**.

If, on the other hand, we express the equilibrium by the following symbol:

$$Na_2SO_4+2HNO_3 \rightleftarrows H_2SO_4+2NaNO_3,$$

Guldberg and Waage would have:

$$\log C_{Na_2SO_4}+2\log C_{HNO_3}-\log C_{H_2SO_4}-2\log C_{NaNO_3}=K;$$

while we obtain:

$$\log C_{Na_2SO_4}+2.03\log C_{HNO_3}-1.07\log C_{H_2SO_4}$$
$$-1.91\log C_{NaNO_3}=K;$$

thus, again, an almost perfect agreement.

4. The investigations of Ostwald* on the action of hydrochloric acid on zinc sulphide, which relate to the equilibrium expressed by the following symbol:

$$ZnS+2HCl \rightleftarrows H_2S+ZnCl_2,$$

leads us, by taking into account the fact that:

$$i_{HCl}=1.98,\ i_{H_2S}=1.04,\ i_{ZnCl_2}=2.53,$$

to the relation:

$$3.96\log C_{HCl}-1.04\log C_{H_2S}-2.53\log C_{ZnCl_2}=K.$$

Where at the beginning only hydrochloric acid and zinc sulphide were present, the concentrations of hydrogen sulphide and zinc chloride in this series of experiments are evidently equal. The result would then be so expressed that the original concentration of the hydrochloric acid would be given by the volume (V), in which a known amount of this substance was present, while the fraction (x) denoted that portion which, by contact with zinc sulphide, had been finally transformed into zinc chloride. We obtain accordingly:

$$3.96\log\frac{1-x}{V}-3.57\log\frac{x}{V}=\text{constant};$$

and therefore also:

$$\frac{x}{(1-x)^{1.11}}V^{0.11}=\text{constant}.$$

This function appears, in fact, to be nearly constant:

VOLUME (V).	UNTRANSFORMED PART (x).	$\frac{x}{(1-x)^{1.11}}V^{0.11}$.
1.....	0.0411	0.0430
2.....	0.0380	0.0428
4.....	0.0345	0.0418
8.....	0.0317	0.0413

* *Journ. prakt. Chem.*, (2), **19**, 480.

The analogous experiments with sulphuric acid, where i for H_2SO_4 and $ZnSO_4$ is 2.06 and 0.98 respectively, gave, similarly:

$$\frac{x}{(1-x)^{1.02}} V^{0.02} = \text{constant},$$

which amounts, therefore, to nearly a constant value for x. This is also, in fact, the experimental result, as is shown by the following table:

VOLUME (V).	UNTRANSFORMED PART (x).
2	0.0238
4	0.0237
8	0.0240
16	0.0241

5. The experiments of Engel* also merit consideration. In these, the question is as to the solubility of magnesium carbonate in water containing carbon dioxide, therefore of the following equilibrium:

$$MgCO_3 + H_2CO_3 \rightleftarrows Mg(HCO_3)_2.$$

Since i for magnesium dicarbonate is 2.64, our formula leads here to the following relation:

$$0.379 \log C_{H_2CO_3} - \log C_{Mg(HCO_3)_2} = K;$$

while that observed was:

$$0.37 \log C_{H_2CO_3} - \log C_{Mg(HCO_3)_2} = K.$$

6. The experiments of the same author,† on the simultaneous solubility of ammonium and copper sulphates, should also be mentioned here, in which we have to deal essentially with the equilibrium:

$$CuSO_4 + (NH_4)_2SO_4 \rightleftarrows (NH_4)_2Cu(SO_4)_2.$$

Since the double salt was always present partially undissolved, and since i for $CuSO_4$ and $(NH_4)_2SO_4$ is 0.98 and 2, respectively, we obtain here the relation:

$$0.49 \log C_{CuSO_4} + \log C_{(NH_4)_2SO_4} = K,$$

while that found was:

$$0.438 \log C_{CuSO_4} + \log C_{(NH_4)_2SO_4} = K.$$

* *Compt. rend.*, **100**, 352, 444.
† *Ibid.*, **102**, 113.

7. Finally, we mention the experiments of Le Chatelier* on the equilibrium between basic mercury sulphate and sulphuric acid, which is expressed by the following symbol:

$$Hg_3SO_6 + 2\,H_2SO_4 \rightleftarrows 3\,HgSO_4 + 2\,H_2O.$$

In this case, where i for H_2SO_4 and $HgSO_4$ is 2.06 and 0.98, respectively, we expect the following relation:

$$1.4 \log C_{H_2SO_4} - \log C_{HgSO_4} = K,$$

while that observed was:

$$1.58 \log C_{H_2SO_4} - \log C_{HgSO_4} = K.$$

A very satisfactory agreement, in general, is thus indicated.

AMSTERDAM, *September*, 1887.

JACOBUS HENDRICUS VAN'T HOFF was born August 30, 1852, at Rotterdam. He received the degree of Doctor of Philosophy from Utrecht in 1874, having studied at the Polytechnic Institute in Delft from 1869 to 1871, at the University of Leyden in 1871, at Bonn with Kekulé in 1872, with Würtz in Paris in 1873, and with Mulder in Utrecht in 1874.

He was made privat-docent at the veterinary college in Utrecht in 1876, and in 1878 professor of chemistry, mineralogy, and geology at the university in Amsterdam. The latter position he held until about two years ago, when he was called to a chair created for him in the University of Berlin.

Probably the best known work of Van't Hoff is *La Chimie dans l'Espace*, which was the origin of that branch of chemistry which has come to be known as stereochemistry. He pointed out here that whenever a compound is optically active, it always contains at least one "asymmetric" carbon atom, *i. e.*, a carbon atom in combination with four different elements or groups. This book appeared first in Dutch in 1874, a year later in French, and has recently been enlarged and translated into English. Other books by Van't Hoff which should be mentioned are: *Views on Organic Chemistry*, *Ten Years in the History of a Theory*, *Studies in Chemical Dynamics*, revised and enlarged by Cohen, and translated into English by Ewan —one of Van't Hoff's most valuable contributions to science; *Lectures on the Formation and Decomposition of Double Salts*, and *Lectures on Theoretical and Physical Chemistry*, which is just appearing.

* *Compt. rend.*, **97**, 1555.

The number of papers published by Van't Hoff is not very large, indeed, unusually small, for one who is so well known. That on *Solid Solutions and the Determination of the Molecular Weight of Solids,** opened up a field in which a number have subsequently worked.

* *Ztschr. Phys. Chem.*, **5**, 322.

N THE DISSOCIATION OF SUBSTANCES DISSOLVED IN WATER

BY

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Zeitschrift für Physikalische Chemie, **1**, 631, 1887

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THE DISSOCIATION OF SUBSTANCES DISSOLVED IN WATER*

BY

SVANTE ARRHENIUS

· a paper submitted to the Swedish Academy of Sciences, he 14th of October, 1895, Van't Hoff proved experimen-, as well as theoretically, the following unusually significant ralization of Avogadro's law:†

The pressure which a gas exerts at a given temperature, if finite number of molecules is contained in a definite vol-, is equal to the osmotic pressure which is produced by ; substances under the same conditions, if they are dis-ɔd in any given liquid."

ɪn't Hoff has proved this law in a manner which scarcely ɔs any doubt as to its absolute correctness. But a diffi-y which still remains to be overcome, is that the law in tion holds only for "most substances"; a very consider-number of the aqueous solutions investigated furnishing ptions, and in the sense that they exert a much greater otic pressure than would be required from the law re-ɔd to.

a gas shows such a deviation from the law of Avogadro, ɜ explained by assuming that the gas is in a state of dis-ation. The conduct of chlorine, bromine, and iodine, at ıer temperatures is a very well-known example. We re-l these substances under such conditions as broken down simple atoms.

Ztschr. Phys. Chem., **1**, 631, 1887.

†Van't Hoff, *Une propriété générale de la matière diluée*, p. 48; *Sv. Vk-s Handlingar*, **21**, Nr. 17, 1886. [Also in *Archives Néerlandaises* 885.]

The same expedient may, of course, be made use of to explain the exceptions to Van't Hoff's law; but it has not been put forward up to the present, probably on account of the newness of the subject, the many exceptions known, and the vigorous objections which would be raised from the chemical side, to such an explanation. The purpose of the following lines is to show that such an assumption, of the dissociation of certain substances dissolved in water, is strongly supported by the conclusions drawn from the electrical properties of the same substances, and that also the objections to it from the chemical side are diminished on more careful examination.

In order to explain the electrical phenomena we must assume with Clausius* that some of the molecules of an electrolyte are dissociated into their ions, which move independently of one another. But since the "osmotic pressure" which a substance dissolved in a liquid exerts against the walls of the confining vessel, must be regarded, in accordance with the modern kinetic view, as produced by the impacts of the smallest parts of this substance, as they move, against the walls of the vessel, we must, therefore, assume, in accordance with this view, that a molecule dissociated in the manner given above, exercises as great a pressure against the walls of the vessel as its ions would do in the free condition. If, then, we could calculate what fraction of the molecules of an electrolyte is dissociated into ions, we should be able to calculate the osmotic pressure from Van't Hoff's law.

In a former communication "On the Electrical Conductivity of Electrolytes," I have designated those molecules whose ions are independent of one another in their movements, as active; the remaining molecules, whose ions are firmly combined with one another, as inactive. I have also maintained it as probable, that in extreme dilution all the inactive molecules of an electrolyte are transformed into active.† This assumption I will make the basis of the calculations now to be carried out. I have designated the relation between the number of active molecules and the sum of the active and inactive molecules, as the activity coefficient.‡ The activity coefficient of an

* Clausius, *Pogg. Ann.*, **101**, 347 (1857); *Wied. Elektr.*, **2**, 941.

† *Bihang der Stockholmer Akademie*, **8**, Nr. 13 and 14, 2 Tl. pp. 5 and 13; 1 Tl., p. 61.

‡ *l. c.*, 2 Tl., p. 5.

electrolyte at infinite dilution is therefore taken as *unity*. For smaller dilution it is less than *one*, and from the principles established in my work already cited, it can be regarded as equal to the ratio of the actual molecular conductivity of the solution to the maximum limiting value which the molecular conductivity of the same solution approaches with increasing dilution. This obtains for solutions which are not too concentrated (*i. e.*, for solutions in which disturbing conditions, such as internal friction, etc., can be disregarded).

If this activity coefficient (α) is known, we can calculate as follows the values of the coefficient i tabulated by Van't Hoff. i is the relation between the osmotic pressure actually exerted by a substance and the osmotic pressure which it would exert if it consisted only of inactive (undissociated) molecules. i is evidently equal to the sum of the number of inactive molecules, plus the number of ions, divided by the sum of the inactive and active molecules. If, then, m represents the number of inactive, and n the number of active molecules, and k the number of ions into which every active molecule dissociates (*e. g.*, $k=2$ for KCl, *i. e.*, K and Cl; $k=3$ for $BaCl_2$ and K_2SO_4, *i. e.*, Ba, Cl, Cl, and K, K, SO_4), then we have :

$$i=\frac{m+kn}{m+n}.$$

But since the activity coefficient (α) can, evidently, be written $\frac{n}{m+n}$:

$$i=1+(k-1)\alpha.$$

Part of the figures given below (those in the last column), were calculated from this formula.

On the other hand, i can be calculated as follows from the results of Raoult's experiments on the freezing-point of solutions, making use of the principles stated by Van't Hoff. The lowering (t) of the freezing-point of water (in degrees Celsius), produced by dissolving a gram-molecule of the given substance in one litre of water, is divided by 18.5. The values of i thus calculated, $i=\frac{t}{18.5}$, are recorded in next to the last column. All the figures given below are calculated on the assumption that one gram of the substance to be investigated was dissolved in one litre of water (as was done in the experiments of Raoult).

BASES—(*continued*).

SUBSTANCE.	FORMULA.	a	$i=\frac{t}{18.5}$	$i=1+(k-1)a.$
Tetraethylammonium hydrate	$(C_2H_5)_4NOH$	0.92	——	1.92
Ammonia	NH_3	0.01	1.03	1.01
Methylamine	CH_3NH_2	0.03	1.00	1.03
Trimethylamine	$(CH_3)_3N$	0.03	1.09	1.03
Ethylamine	$C_2H_5NH_2$	0.04	1.00	1.04
Propylamine	$C_3H_7NH_2$	0.04	1.00	1.04
Aniline	$C_6H_5NH_2$	0.00	0.83	1.00

ACIDS.

SUBSTANCE.	FORMULA.	a	$i=\frac{t}{18.5}$	$i=1+(k-1)a.$
Hydrochloric acid	HCl	0.90	1.98	1.90
Hydrobromic acid	HBr	0.94	2.03	1.94
Hydroiodic acid	HI	0.96	2.03	1.96
Hydrofluosilicic acid	H_2SiF_6	0.75	2.46	1.75
Nitric acid	HNO_3	0.92	1.94	1.92
Chloric acid	$HClO_3$	0.91	1.97	1.91
Perchloric acid	$HClO_4$	0.94	2.09	1.94
Sulphuric acid	H_2SO_4	0.60	2.06	2.19
Selenic acid	H_2SeO_4	0.66	2.10	2.31
Phosphoric acid	H_3PO_4	0.08	2.32	1.24
Sulphurous acid	H_2SO_3	0.14	1.03	1.28
Hydrogen sulphide	H_2S	0.00	1.04	1.00
Iodic acid	HIO_3	0.73	1.30	1.73
Phosphorous acid	$P(OH)_3$	0.46	1.29	1.46
Boric acid	$B(OH)_3$	0.00	1.11	1.00
Hydrocyanic acid	HCN	0.00	1.05	1.00
Formic acid	$HCOOH$	0.03	1.04	1.03
Acetic acid	CH_3COOH	0.01	1.03	1.01
Butyric acid	C_3H_7COOH	0.01	1.01	1.01
Oxalic acid	$(COOH)_2$	0.25	1.25	1.49
Tartaric acid	$C_4H_6O_6$	0.06	1.05	1.11
Malic acid	$C_4H_6O_5$	0.04	1.08	1.07
Lactic acid	$C_3H_6O_3$	0.03	1.01	1.03

SALTS.

SUBSTANCE.	FORMULA.	a	$i=\frac{t}{18.5}$	$i=1+(k-1)a.$
Potassium chloride....	KCl	0.86	1.82	1.86
Sodium chloride.....	$NaCl$	0.82	1.90	1.82
Lithium chloride.....	$LiCl$	0.75	1.99	1.75
Ammonium chloride...	NH_4Cl	0.84	1.88	1.84
Potassium iodide.....	KI	0.92	1.90	1.92
Potassium bromide....	KBr	0.92	1.90	1.92
Potassium cyanide.....	KCN	0.88	1.74	1.88
Potassium nitrate.....	KNO_3	0.81	1.67	1.81
Sodium nitrate.....	$NaNO_3$	0.82	1.82	1.82
Ammonium nitrate....	NH_4NO_3	0.81	1.73	1.81
Potassium acetate.....	CH_3COOK	0.83	1.86	1.83
Sodium acetate.....	CH_3COONa	0.79	1.73	1.79
Potassium formate.....	$HCOOK$	0.83	1.90	1.83
Silver nitrate.....	$AgNO_3$	0.86	1.60	1.86
Potassium chlorate....	$KClO_3$	0.83	1.78	1.83
Potassium carbonate...	K_2CO_3	0.69	2.26	2.38
Sodium carbonate.....	Na_2CO_3	0.61	2.18	2.22
Potassium sulphate....	K_2SO_4	0.67	2.11	2.33
Sodium sulphate.....	Na_2SO_4	0.62	1.91	2.24
Ammonium sulphate...	$(NH_4)_2SO_4$	0.59	2.00	2.17
Potassium oxalate.....	$K_2C_2O_4$	0.66	2.43	2.32
Barium chloride.....	$BaCl_2$	0.77	2.63	2.54
Strontium chloride....	$SrCl_2$	0.75	2.76	2.50
Calcium chloride.....	$CaCl_2$	0.75	2.70	2.50
Cupric chloride.....	$CuCl_2$	——	2.58	——
Zinc chloride.....	$ZnCl_2$	0.70	——	2.40
Barium nitrate.....	$Ba(NO_3)_2$	0.57	2.19	2.13
Strontium nitrate.....	$Sr(NO_3)_2$	0.62	2.23	2.23
Calcium nitrate.....	$Ca(NO_3)_2$	0.67	2.02	2.33
Lead nitrate.....	$Pb(NO_3)_2$	0.54	2.02	2.08
Magnesium sulphate...	$MgSO_4$	0.40	1.04	1.40
Ferrous sulphate.....	$FeSO_4$	0.35	1.00	1.35
Copper sulphate.....	$CuSO_4$	0.35	0.97	1.35
Zinc sulphate.....	$ZnSO_4$	0.38	0.98	1.38
Cupric acetate.....	$(C_2H_3O_2)_2Cu$	0.33	1.68	1.66
Magnesium chloride...	$MgCl_2$	0.70	2.64	2.40
Mercuric chloride.....	$HgCl_2$	0.03	1.11	1.05
Cadmium iodide.....	CdI_2	0.28	0.94	1.56
Cadmium nitrate.....	$Cd(NO_3)_2$	0.73	2.32	2.46
Cadmium sulphate....	$CdSO_4$	0.35	0.75	1.35

The last three numbers in next to the last column are not taken, like all the others, from the work of Raoult,* but from the older data of Rüdorff,† who employed in his experiments very large quantities of the substance investigated, therefore no very great accuracy can be claimed for these three numbers. The value of α is calculated from the results of Kohlrausch,‡ Ostwald§ (for acids and bases), and some few from those of Grotrian‖ and Klein.¶ The values of α, calculated from the results of Ostwald, are by far the most certain, since the two quantities which give α can, in this case, be easily determined with a fair degree of accuracy. The errors in the values of i, calculated from such values of α, cannot be more than 5 per cent. The values of α and i, calculated from the data of Kohlrausch, are somewhat uncertain, mainly because it is difficult to calculate accurately the maximum value of the molecular conducting power. This applies, to a still greater extent, to the values of α and i calculated from the experimental data of Grotrian and Klein. The latter may contain errors of from 10 to 15 per cent. in unfavorable cases. It is difficult to estimate the degree of accuracy of Raoult's results. From the results themselves, for very nearly related substances, errors of 5 per cent., or even somewhat more, do not appear to be improbable.

It should be observed that, for the sake of completeness, all substances are given in the above table for which even a fairly accurate calculation of i by the two methods was possible. If now and then data are wanting for the conductivity of a substance (cupric chloride and tetramethylammonium hydrate), such are calculated, for the sake of comparison, from data for a very nearly related substance (zinc chloride and tetraethylammonium hydrate), whose electrical properties cannot differ appreciably from those of the substance in question.

Among the values of i which show a very large difference from one another, those for hydrofluosilicic acid must be

* Raoult, *Ann. Chim. Phys.*, [5], **28**, 133 (1883); [6], **2**, 66, 99, 115 (1884); [6], **4**, 401 (1885). [*This volume*, p. 52.]

† Rüdorff, Ostwald's *Lehrb. all. Chem.*, I., 414.

‡ Kohlrausch, *Wied. Ann.*, **6**, 1 and 145 (1879); **26**, 161 (1885).

§ Ostwald, *Journ. prakt. Chem.*, [2], **32**, 300 (1885); [2], **33**, 352 (1886); *Ztschr. Phys. Chem.*, **1**, 74 and 97 (1887).

‖ Grotrian, *Wied. Ann.*, **18**, 177 (1883).

¶ Klein, *Wied. Ann.*, **27**, 151 (1886).

especially mentioned. But Ostwald has, indeed, shown that in all probability, this acid is partly broken down in aqueous solution into $6HF$ and SiO_2, which would explain the large value of i given by the Raoult method.

There is one condition which interferes, possibly very seriously, with directly comparing the figures in the last two columns—namely, that the values really hold for different temperatures. All the figures in next to the last column hold, indeed, for temperatures only a very little below 0°C., since they were obtained from experiments on inconsiderable lowerings of the freezing-point of water. On the other hand, the figures of the last column for acids and bases (Ostwald's experiments) hold at 25°, the others at 18°. The figures of the last column for non-conductors hold, of course, also at 0°C., since these substances at this temperature do not consist, to any appreciable extent, of dissociated (active) molecules.

An especially marked parallelism appears,* beyond doubt, on comparing the figures in the last two columns. This shows, *a posteriori*, that in all probability the assumptions on which I have based the calculation of these figures are, in the main, correct. These assumptions were:

1. That Van't Hoff's law holds not only for *most*, but for *all substances*, even for those which have hitherto been regarded as exceptions (electrolytes in aqueous solution).

2. That every electrolyte (in aqueous solution), consists partly of active (in electrical and chemical relation), and partly of inactive molecules, the latter passing into active molecules on increasing the dilution, so that in infinitely dilute solutions only active molecules exist.

The objections which can probably be raised from the chemical side are essentially the same which have been brought forward against the hypothesis of Clausius, and which I have earlier sought to show, were completely untenable.† A repetition of these objections would, then, be almost superfluous. I will call attention to only one point. Although the dissolved substance exercises an osmotic pressure against the wall of the vessel, just as if it were partly dissociated into its ions, yet

* In reference to some salts which are distinctly exceptions, compare below, p. 55.

† *l. c.*, 2 Tl., pp. 6 and 31.

the dissociation with which we are here dealing is not exactly the same as that which exists when, *e. g.*, an ammonium salt is decomposed at a higher temperature. The products of dissociation in the first case (the ions) are charged with very large quantities of electricity of opposite kind, whence certain conditions appear (the incompressibility of electricity), from which, it follows that the ions cannot be separated from one another to any great extent, without a large expenditure of energy.* On the contrary, in ordinary dissociation where no such conditions exist, the products of dissociation can, in general, be separated from one another.

The above two assumptions are of the very widest significance, not only in their theoretical relation, of which more hereafter, but also, to the highest degree, in a practical sense. If it could, for instance, be shown that the law of Van't Hoff is generally applicable—which I have tried to show is highly probable—the chemist would have at his disposal an extraordinarily convenient means of determining the molecular weight of every substance soluble in á liquid.†

At the same time, I wish to call attention to the fact that the above equation (1) shows a connection between the two values i and α, which play the chief rôles in the two chemical theories developed very recently by Van't Hoff and myself.

I have tacitly assumed in the calculation of i, carried out above, that the inactive molecules exist in the solution as simple molecules and not united into larger molecular complexes. The result of this calculation (*i. e.*, the figures in the last column), compared with the results of direct observation (the figures in next to the last column), shows that, in general, this supposition is perfectly justified. If this were not true the figures in next to the last column would, of course, prove to be smaller than in the last. An exception, where the latter undoubtedly takes place, is found in the group of sulphates of the magnesium series (*Mg* SO_4, *Fe* SO_4, *Cu* SO_4, *Zn* SO_4, and *Cd* SO_4), also in cadmium iodide. We can assume, to explain this, that the inactive molecules of these salts are, in part,

* *l. c.*, 2 Tl., p. 8.

† This means has already been employed. Compare Raoult, *Ann. Chim. Phys.*, [6], **8**, 317 (1886); Paternò and Nasini, *Ber. deutsch. chem. Gesell.*, 1886, 2527.

combined with one another. Hittorf,* as is well known, was led to this assumption for cadmium iodide, through the large change in the migration number. And if we examine his tables more closely we will find, also, an unusually large change of this number for the three of the above-named sulphates ($Mg\ SO_4$, $Cu\ SO_4$, and $Zn\ SO_4$) which he investigated. It is then very probable that this explanation holds for the salts referred to. But we must assume that double molecules exist only to a very slight extent in the other salts. It still remains, however, to indicate briefly the reasons which have led earlier authors to the assumption of the general existence of complex molecules in solution.

Since, in general, substances in the gaseous state consist of simple molecules (from Avogadro's law), and since a slight increase in the density of gases often occurs near the point of condensation, indicating a union of the molecules, we are inclined to see in the change of the state of aggregation, such combinations taking place to a much greater extent. That is, we assume that the liquid molecules in general are not simple. I will not combat the correctness of this conclusion here. But a great difference arises if this liquid is dissolved in another (*e. g.*, $H\ Cl$ in water). For if we assume that by dilution the molecules which were inactive at the beginning become active, the ions being separated to a certain extent from one another, which of course requires a large expenditure of energy, it is not difficult to assume, also, that the molecular complexes break down, for the most part, on mixing with water, which in any case does not require very much work. The consumption of heat on diluting solutions has been interpreted as a proof of the existence of molecular complexes.† But, as stated, this can also be ascribed to the conversion of inactive into active molecules. Further, some chemists, to support the idea of constant valence, would assume‡ molecular complexes, in which the unsaturated bonds could become saturated. But the doctrine of constant valence is so much disputed that we are scarcely justified in basing any conclusions upon it. The conclusions thus arrived at, that, *e.g.*, potassium chloride would have the formula $(KCl)_3$, L. Meyer

* Hittorf, *Pogg. Ann.*, **106**, 547 and 551 (1859); *Wied. Elektr.*, **2**, 584.

† Ostwald, *Lebrb. all. Chem.*, I., 811; L. Meyer, *Moderne Theorien der Chemie*, p. 319 (1880).

‡ L. Meyer, *l. c.* p. 360.

sought to support by the fact that potassium chloride is much less volatile than mercuric chloride, although the former has a much smaller molecular weight than the latter. Independent of the theoretical weakness of such an argument, this conclusion could, of course, hold only for the pure substances, not for solutions. Several other reasons have been brought forward by L. Meyer for the existence of molecular complexes, *e. g.*, the fact that sodium chloride diffuses more slowly than hydrochloric acid,* but this is probably to be referred to the greater friction (according to electrical determinations), of sodium against water, than of hydrogen. But it suffices to cite L. Meyer's own words: "Although all of these different points of departure for ascertaining molecular weights in the liquid condition are still so incomplete and uncertain, nevertheless they permit us to hope that it will be possible in the future to ascertain the size of molecules."† But the law of Van't Hoff gives entirely reliable points of departure, and these show that in almost all cases the number of molecular complexes in solutions can be disregarded, while they confirm the existence of such in some few cases, and, indeed, in those in which there were formerly reasons for assuming the existence of such complexes.‡ Let us, then, not deny the possibility that such molecular complexes also exist in solutions of other salts—and especially in concentrated solutions; but in solutions of such dilution as was investigated by Raoult, they are, in general, present in such small quantity that they can be disregarded without appreciable error in the above calculations.

Most of the properties of dilute solutions of salts are of a so-called additive nature. In other words, these properties (expressed in figures) can be regarded as a sum of the properties of the parts of the solution (of the solvent, and of the parts of the molecules, which are, indeed, the ions). As an example, the conductivity of a solution of a salt can be regarded as the sum of the conductivities of the solvent (which in most cases is zero), of the positive ion, and of the negative ion.§ In most cases this is controlled by comparing two salts of one

* L. Meyer, *l. c.* p. 316.

† L. Meyer, *l. c.* p. 321. The law of Van't Hoff makes this possible, as is shown above.

‡ Hittorf, *l. c.* Ostwald's *Lehrb. all. Chem.*, p. 816.

§ Kohlrausch, *Wied. Ann.*, 167 (1879).

acid (*e. g.*, potassium and sodium chlorides) with two corresponding salts of the same metals with another acid (*e. g.*, potassium and sodium nitrates). Then the property of the first salt (KCl), *minus* the property of the second ($NaCl$), is equal to the property of the third (KNO_3), *minus* the property of the fourth ($NaNO_3$). This holds in most cases for several properties, such as conductivity, lowering of freezing-point, refraction equivalent, heat of neutralization, etc., which we will treat briefly, later on. It finds its explanation in the nearly complete dissociation of most salts into their ions, which was shown above to be true. If a salt (in aqueous solution) is completely broken down into its ions, most of the properties of this salt can, of course, be expressed as the sum of the properties of the ions, since the ions are independent of one another in most cases, and since every ion has, therefore, a characteristic property, independent of the nature of the opposite ion with which it occurs. The solutions which we, in fact, investigate are never completely dissociated, so that the above statement does not hold rigidly. But if we consider such salts as are 80 to 90 per cent. dissociated (salts of the strong bases with the strong acids, almost without exception), we will, in general, not make very large errors if we calculate the properties on the assumption that the salts are completely broken down into their ions. From the above table this evidently holds also for the strong bases and acids: $Ba(OH)_2$, $Sr(OH)_2$, $Ca(OH)_2$, $LiOH$, $NaOH$, KOH, $TlOH$, and HCl, HBr, HI, HNO_3, $HClO_3$, and $HClO_4$.

But there is another group of substances which, for the most part, have played a subordinate rôle in the investigations up to the present, and which are far from completely dissociated, even in dilute solutions. Examples taken from the above table are, the salts, $HgCl_2$ (and other salts of mercury), CdI_2, $CdSO_4$, $FeSO_4$, $MgSO_4$, $ZnSO_4$, $CuSO_4$, and $Cu(C_2H_3O_2)_2$; the weak bases and acids, as NH_3, and the different amines, H_3PO_4, H_2S, $B(OH)_3$, HCN, formic, acetic, butyric, tartaric, malic, and lactic acids. The properties of these substances will not, in general, be of the same (additive) nature as those of the former class, a fact which is completely confirmed, as we will show later. There are, of course, a number of substances lying between these two groups, as is also shown by the above table. Let attention be here called to the fact that several

investigators have been led to the assumption of a certain kind of complete dissociation of salts into their ions, by considering that the properties of substances of the first group, which have been investigated far more frequently than those of the second, are almost always of an additive nature.* But since no reason could be discovered from the chemical side why salt molecules should break down (into their ions) in a perfectly definite manner, and, moreover, since chemists, for certain reasons not to be more fully considered here, have fought as long as possible against the existence of so-called unsaturated radicals (under which head the ions must be placed), and since, in addition, it cannot be denied that the grounds for such an assumption were somewhat uncertain,† the assumption of complete dissociation has not met with any hearty approval up to the present. The above table shows, also, that the aversion of the chemist to the idea advanced, of complete dissociation, has not been without a certain justification, since at the dilutions actually employed, the dissociation is never complete, and even for a large number of electrolytes, (the second group) is relatively inconsiderable.

After these observations we now pass to the special cases in which additive properties occur.

1. *The Heat of Neutralization in Dilute Solutions.*—When an acid is neutralized with a base, the energies of these two substances are set free in the form of heat; on the other hand, a certain amount of heat disappears as such, equivalent to the energies of the water and salt (ions) formed. We designate with ( ) the energies for those substances, for which it is unimportant for the deduction whether they exist as ions or not, and with [ ] the energies of the ions, which always means the energies in dilute solution. To take an example, the following amounts of heat are set free on neutralizing $Na\,OH$ with $\frac{1}{2}\,H_2SO_4$ (1), and with $H\,Cl$ (2), and on neutralizing $K\,OH$ with $\frac{1}{2}\,H_2SO_4$ (3), and with $H\,Cl$ (4) (all in equivalent quantities, and on the previous assumption of a complete dissociation of the salts):

* Valson, *Compt. rend.*, **73**, 441 (1871); **74**, 103 (1872); Favre and Valson, *Compt. rend.*, **75**, 1033 (1872); Raoult, *Ann. Chim. Phys.*, [6], 4, 426.

† In reference to the different hypotheses of Raoult, compare, *l. c.*, p. 401.

$(Na\,OH)+\frac{1}{2}(H_2SO_4)-(H_2O)-[Na]-[\frac{1}{2}SO_4]$. (1)
$(Na\,OH)+(H\,Cl)-(H_2O)-[Na]-[Cl]$. (2)
$(K\,OH)+\frac{1}{2}(H_2SO_4)-(H_2O)-[K]-[\frac{1}{2}SO_4]$. (3)
$(K\,OH)+(H\,Cl)-(H_2O)-[K]-[Cl]$. (4)

(1)—(2) is, of course, equal to (3)—(4), on the assumption of a complete dissociation of the salts. This holds, approximately, as above indicated, in the cases which actually occur. This is all the more true, since the salts which are farthest removed from complete dissociation—in this case Na_2SO_4 and K_2SO_4—are dissociated to approximately the same extent, therefore the errors in the two members of the last equation are approximately of equal value, a condition which, in consequence of the additive properties, exists more frequently than we could otherwise expect. The small table given below shows that the additive properties distinctly appear on neutralizing strong bases with strong acids. This is no longer the case with the salts of weak bases with weak acids, because they are, in all probability, partly decomposed by the water.

HEATS OF FORMATION OF SOME SALTS IN DILUTE SOLUTION, ACCORDING TO THOMSEN AND BERTHELOT.

	HCl HBr HI	HNO_3	$C_2H_4O_2$	CH_2O_2	$\frac{1}{2}(COOH)_2$
$NaOH$....	13.7	13.7 (0.0)	13.3 (−0.4)	13.4 (−0.3)	14.3 (+0.6)
KOH.....	13.7	13.8 (+0.1)	13.3 (−0.4)	13.4 (−0.3)	14.3 (+0.6)
NH_3.....	12 4	12.5 (+0.1)	12.0 (−0.4)	11.9 (−0.5)	12.7 (+0.3)
$\frac{1}{2}Ca(OH)_2$.	14.0	13.9 (−0.1)	13.4 (−0.6)	13.5 (−0.5)	——
$\frac{1}{2}Ba(OH)_2$	13.8	13.9 (+0.1)	13.4 (−0 4)	13.5 (−0.3)	——
$\frac{1}{2}Sr(OH)_2$.	14.1	13.9 (−0.2)	13.3 (−0.8)	13.5 (−0.6)	——

	$\frac{1}{2}H_2SO_4$	$\frac{1}{2}H_2S$	HCN	$\frac{1}{2}CO_2$
$NaOH$.....	15.8 (+2.1)	3.8 (−9.9)	2.9 (−10.8)	10.2 (−3.5)
KOH.....	15.7 (+2.0)	3.8 (−9.9)	3 0 (−10.7)	10.1 (−3.6)
NH_3.....	14.5 (+2.0)	3.1 (−9.3)	1.3 (−11.1)	5.3 (−7.1)
$\frac{1}{2}Ca(OH)_2$..	——	3.9 (−10.1)	——	——
$\frac{1}{2}Ba(OH)_2$..	——	——	——	——
$\frac{1}{2}Sr(OH)_2$..	——	——	——	——

As can be seen from the figures inclosed in brackets (which represent the difference between the heat tone in question and the corresponding heat tone of the chloride), they are approxi-

mately constant in every vertical column. This fact is very closely connected with the so-called thermo-neutrality of salts; but since I have previously treated this subject more directly, and have emphasized its close connection with the Williamson-Clausius* hypothesis, I do not now need to give a detailed analysis of it.

2. *Specific Volume and Specific Gravity of Dilute Salt Solutions.*—If a small amount of salt, whose ions can be regarded as completely independent of one another in the solution, is added to a litre of water, the volume of this is changed. Let x be the quantity of the one ion added, and y that of the other, the volume will be approximately equal to $(1+ax+by)$ litres, a and b being constants. But since the ions are dissociated from one another, the constant a of the one ion will, of course, be independent of the nature of the other ion. The weight is, similarly, $(1+cx+dy)$ kilograms, in which c and d are two other constants characteristic for the ions. The specific gravity will then, for small amounts of x and y, be represented by the formula:

$$1+(c-a)x+(b-d)y,$$

where, of course, $(c-a)$ and $(b-d)$ are also characteristic constants for the two ions. The specific gravity is, then, an additive property for dilute solutions, as Valson† has also found. But since "specific gravity is not applicable to the representation of stöichiometric laws," as Ostwald‡ maintains, we will refrain from a more detailed discussion of these results. The determination of the constants a and b, etc., promises much of value, but thus far has not been carried out.

The changes in volume in neutralization are closely related to these phenomena. It can be shown that the change in volume in neutralization is an additive property, from considerations very similar to those above for heat of neutralization. All the salts investigated (K_1- Na- NH_4-) are almost completely dissociated in dilute solutions, as is clear from the above table (and is even clearer from the subsequent work of Ostwald), so that a very satisfactory agreement for these salts can be expected. The differences of the change in volume in the

* *l. c.*, 2 Tl., p. 67.

† Valson, *Compt. rend.*, **73**, 441 (1871); Ostwald, *Lehrb. all. Chem.*, I., 384.

‡ Ostwald, *ibid.*, I., 386.

formation of the salts in question, from nineteen different acids, are also found to be nearly constant numbers.* Since bases which form salts of the second group have not been investigated, there are no exceptions known.

3. *Specific Refractivity of Solutions.*—If we represent by n the index of refraction, by d the density, and by P the weight of a substance, $P\frac{n-1}{d}$ is, as is well known, a value which, when added for the different parts of mixtures of several substances, gives the corresponding value for the mixture. Consequently, this value must make the refraction equivalent an additive property also for the dissociated salts. The investigations of Gladstone have shown distinctly that this is true. The potassium and sodium salts have been investigated in this case just as the acids themselves. We take the following short table on molecular refraction equivalents from the *Lehrbuch* of Ostwald:†

	POTASSIUM.	SODIUM.	HYDROGEN.	$K-Na$.	$K-H$.
Chloride.....	18.44	15.11	14.44	3.3	4.0
Bromide.....	25.34	21.70	20.63	3.6	4.7
Iodide.....	35.33	31.59	31.17	3.7	4.2
Nitrate.....	21.80	18.66	17.24	3.1	4.5
Sulphate....	30.55	——	22.45	——	2×4.1
Hydrate.....	12.82	9.21	5.95	3.6	6.8
Formate.....	19.93	16.03	13.40	3.9	6.5
Acetate.....	27.65	24.05	21.20	3.6	6.5
Tartrate.....	57.60	50.39	45.18	2×3.6	2×6.2

The difference $K-Na$ is, as is seen, almost constant throughout, which was also to be expected from the knowledge of the extent of dissociation of the potassium and sodium salts. The same holds also for the difference $K-H$, as long as we are dealing with the strong (dissociated) acids. On the contrary, the substances of the second group (the slightly dissociated acids), behave very differently, the difference $K-H$ being much greater than for the first group.

4. Valson‡ believed that he also found additive properties

* Ostwald, *Lehrb. all. Chem.*, I., 388.

† Ostwald, *l. c.*, p. 443.

‡ Valson, *Compt. rend.*, **74**, 103 (1872); Ostwald, *l. c.* p. 492.

of salt solutions in *Capillary Phenomena*. But since this can be traced back to the fact that the specific gravity is an additive property, as above stated, we need not stop to consider it.

5. *Conductivity.*—F. Kohlrausch, as is well known, has done a very great service for the development of the science of electrolysis, by showing that conductivity is an additive property.* Since we have already pointed out how this is to be understood, we pass at once to the data obtained. Kohlrausch gives in his work already cited, the following values for dilute solutions:

$K=48$, $NH_4=47$, $Na=31$, $Li=21$, $Ag=40$, $H=278$, $Cl=49$, $Br=53$, $I=53$, $CN=50$, $OH=141$, $F=30$, $NO_3=46$, $Cl\,O_3=40$, $C_2\,H_3\,O_2=23$, $\frac{1}{2}\,Ba=29$, $\frac{1}{2}\,Sr=28$, $\frac{1}{2}\,Ca=26$, $\frac{1}{2}\,Mg=23$, $\frac{1}{2}\,Zn=20$, $\frac{1}{2}\,Cu=29$.

But these values hold only for the most strongly dissociated substances (salts of the monobasic acids and the strong acids and bases). For the somewhat less strongly dissociated sulphates and carbonates of the univalent metals (compare above table), he obtained, indeed, much smaller values: $K=40$, $NH_4=37$, $Na=22$, $Li=11$, $Ag=32$, $H=166$, $\frac{1}{2}\,SO_4=40$, $\frac{1}{2}\,CO_3=36$; and for the least dissociated sulphates (the metals of the magnesium series), he obtained the following still smaller values: $\frac{1}{2}\,Mg=14$, $\frac{1}{2}\,Zn=12$, $\frac{1}{2}\,Cu=12$, $\frac{1}{2}\,SO_4=22$.

It appears, then, that the law of Kohlrausch holds only for the most strongly dissociated salts, the less strongly dissociated giving very different values. But since the number of active molecules also increases with increase in dilution, so that at extreme dilution all salts break down completely into active (dissociated) molecules, it would be expected that, at higher dilutions, the salts would behave more regularly. I showed, also, from some examples that "we must not lay too much stress upon the anomalous behavior of salts (acetates and sulphates) of the magnesium series, since these anomalies disappear at greater dilutions."† I also believed I could establish the view that conductivity is an additive property,‡ and I ascribed to the conductivity of hydrogen in all acids (even in the poorest conducting, whose behavior was not at all compatible with this view), a value which was entirely independent of the

* Kohlrausch, *Wied. Ann.*, **6**, 167 (1879); *Wied. Elek.*, **1**, 610; **2**, 955.
† *l. c.*, 1 Tl., p. 41.
‡ *l. c.*, 2 Tl., p. 12.

nature of the acid. This, again, was accomplished only with the aid of the conception of activity. The correctness of this view appears still more clearly from the later work of Kohlrausch,* and of Ostwald.† Ostwald attempts to show in his last work upon this subject, that the view that conductivity is additive is tenable without the aid of the activity conception, and he succeeds very well for the salts which he employed (potassium, sodium, and lithium), because these are, in general, very nearly completely dissociated, and especially at very great dilutions. This result receives further support from the fact that analogous salts of the univalent metals, if they are very closely related to one another, are dissociated to approximately the same extent at the same concentrations. But if we were dealing with salts of less closely related metals we should obtain very different results, as is shown distinctly by previous investigations. As Ostwald‡ himself says, the law of Kohlrausch does not hold for the acids, but we must add to it the conception of activity if we would have it hold true. But this law does not apply to all salts. A closer investigation of copper acetate would, indeed, lead to considerable difficulties.§ This would be still more pronounced if we took into account the mercury salts, since it appears from the investigations of Grotrian,‖ as if these gave only a very small fraction of the conductivity derived from this law, even in extreme dilutions. It is apparent that not all of the salts of the univalent metals conform to this law, since, according to Bouty,¶ potassium antimonyl tartrate, in 0.001 normal solution, conducts only about one-fifth as well as potassium chloride. From the law of Kohlrausch it must conduct at least half as well as potassium chloride. But if we make use of the activity conception, the law of Kohlrausch holds very satisfactorily, as is shown by the values of i in the above table for weak bases and acids, calculated on the basis of this law, and also for $Hg\,Cl_2$ and $Cu\,(C_2\,H_3\,O_2)_2$. They agree very well with the values of i derived from the experiments of Raoult.

* Kohlrausch, *Wied. Ann.*, **26**, 215 and 216 (1885).
† Ostwald, *Ztschr. Phys. Chem.*, **1**, 74 and 97 (1887).
‡ Ostwald, *l. c.* p. 79.
§ My work, already cited. 1 Tl., p. 39.
‖ Grotrian, *Wied. Ann.*, **18**, 177 (1883).
¶ Bouty, *Ann. Chim. Phys.*, [6], **3**, 472 (1884).

6. *Lowering of the Freezing-Point.*—Raoult* shows, in one of his investigations, that the lowering of the freezing-point of water by salts can be regarded as an additive property, as would be expected, in accordance with our views for the most strongly dissociated salts in dilute solutions. The following values were obtained for the activities of the ions:

GROUP.		
1st.	Univalent (electro) negative ions (radicals)..	20 (*Cl, Br, OH, NO_3*, etc.)
2d.	Bivalent " " "	11 (*SO_4, $Cr O_4$*, etc.)
3d.	Univalent (electro) positive " "	15 (*H, K, Na, NH_4*, etc.)
4th.†	Bivalent or polyvalent " " "	8 (*Ba, Mg, Al_2*, etc.)

But there are very many exceptions which appear because of unusually small dissociation even in the most dilute solutions, as is seen from the following table:

	Calculated.	Observed.		Calculated.	Observed.
Weak acids.....	35	19	Lead acetate.....	48	22.2
$Cu(C_2H_3O_2)_2$.....	48	31.1	Aluminium acetate.....	128	84.0
Potassium antimonyl tartrate.....	41	18.4	Ferric acetate.....	128	58.1
Mercuric chloride.....	48	20.4	Platinic chloride.....	88	29.0

We know, from experiments on the electrical conductivity of those substances which are given in the first column, that their

* Raoult, *Ann. Chim. Phys.*, [6], **4**, 416 (1885).

† All ions have the same value 18.5, according to the views already explained. Raoult has, evidently, ingeniously forced these substances under the general law of the additivity of freezing-point lowering, by assigning to the ions of the less dissociated substances, as *$Mg SO_4$*, much smaller values (8 and 11 respectively). The possibility of ascribing smaller values to the polyvalent ions is based upon the fact that, in general, the dissociation of salts is smaller the greater the valence of their ions, as I have previously maintained (*l. c.*, 1 Tl., p. 69; 2 Tl., p. 5). "The inactivity (complexity) of a salt solution is greater, the more easily the constituents of the salt (acid and base) form double compounds." This result is, moreover, completely confirmed through subsequent work by Ostwald (*Ztschr. Phys. Chem.*, **1**, 105 to 109). It is evident that if we were to give the correct value, 18.5, to the polyvalent ions, the salts obtained from them would form very distinct exceptions. (Probably a similar view in reference to other additive properties could be correctly brought forward.) Although Raoult has, then, artificially forced these less strongly dissociated salts to conform to his law, he has not succeeded in doing so with all of the salts, as is pointed out above.

molecules are very slightly dissociated. The remaining substances are closely related to these, so that we can expect them to behave similarly, although they have not been investigated, electrically, up to the present. But if we accept the point of view which I have brought forward, all of these substances, the latter as well as the cases previously cited, are not to be regarded as exceptions; on the contrary, they obey exactly the same laws as the other substances hitherto regarded as normal.

Several other properties of salt solutions are closely connected with the lowering of the freezing-point, as Guldberg* and Van't Hoff† have shown. These properties are proportional to the lowering of the freezing-point. All of these properties —lowering of the vapor-pressure, osmotic pressure, isotonic coefficients,—are, therefore, to be regarded as additive. De Vries‡ has also shown this for isotonic coefficients. But since all of these properties can be traced back to the lowering of the freezing-point, I do not think it necessary to enter into the details of them here.

SVANTE ARRHENIUS was born February 19, 1859, near Upsala, Sweden. After leaving the Gymnasium in 1876, he studied in the University of Upsala until 1881. From 1881 to 1883 he worked at the Physical Institute of the Academy of Sciences in Stockholm. Having received the Degree of Doctor of Philosophy from the University of Upsala in 1878, he was appointed privat-docent in that institution in 1884.

A little later, the Stockholm Academy of Sciences granted Arrhenius an allowance that he might visit foreign universities. In 1888 he worked with Van't Hoff in Amsterdam, in 1889 with Ostwald in Leipsic, and in 1890 with Boltzmann in Gratz.

In 1891 he was called to Stockholm as a teacher of physics, in what is termed the Stockholm High School, but which, in reality, corresponds favorably with many of the smaller universities abroad. In 1895 he was appointed to the full professorship of physics in Stockholm, a position which he now holds.

Some of his more important pieces of work, in addition to

* Guldberg, *Compt. rend.*, **70**, 1349 (1870).

† Van't Hoff, *l. c.* p. 20.

‡ De Vries, *Eine Methode zur Analyse der Turgorkraft*, Pringsheim's *Jahrbücher*, **14**, 519 (1883); Van't Hoff, *l. c.* p. 26.

that included in this volume, are: *The Conductivity of Very Dilute Aqueous Solutions* (Dissertation); *Theory of Isohydric Solutions; Effect of the Solar Radiation on the Electrical Phenomena in the Earth's Atmosphere; Effect of the Amount of Carbon Dioxide in the Air on the Temperature of the Earth's Surface.*

Arrhenius is also a member of a number of learned societies and academies.

THE GENERAL LAW OF THE FREEZING OF SOLVENTS

BY

F. M. RAOULT

Professor of Chemistry in Grenoble.

(*Annales de Chimie et de Physique*, [6], **2**, 66, 1884.)

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THE GENERAL LAW OF THE FREEZING OF SOLVENTS*

BY

F. M. RAOULT

IF we represent by A the *coefficient of lowering* of a substance, *i. e.*, the lowering of the freezing-point produced by one gram of the substance dissolved in one hundred grams of the solvent; by M the molecular weight of the compound dissolved, calculated by making in the *atomic* formula of this compound —supposing it to be an anhydride—$H=1$, $O=16$, etc.; by T the *molecular lowering of freezing—i. e.*, the lowering of the freezing-point produced by one molecule† of the substance dissolved in 100 molecules of the solvent, we have:

$$MA=T.$$

I have found that if the solutions are dilute, and do not contain more than one equivalent‡ of substance to a kilogram of water, all the organic substances in aqueous solution produce a molecular lowering which is nearly constant, always lying between 17 and 20, and which usually approaches the mean $T=18.5$; and I have shown (*Ann. Chim. Phys.*, January, 1883) what use could be made of this fact for determining the molecular weights of organic compounds soluble in water. I will now show that analogous results are obtained with all solvents which can be readily solidified, and that a very important general law is connected with them.

In the researches which I shall discuss here, I have generally employed very dilute solutions, containing less than one molecule of substance in two kilograms of water.

* *Ann. Chim. Phys.*, [6], **2**, 66.

† [*By "one molecule" is meant a number of grams of the substance equal to the number expressing its "molecular weight."*]

‡ [*By "equivalent" is meant the same as "molecule."—See above.*]

The use of very dilute solutions offers several advantages. First, it makes it possible to avoid, for the most part, the errors resulting from the more or less arbitrary opinions as to the state of the substance in the solutions, and which result in assigning to the solvent some molecules which, in most cases, belong really to the dissolved substance. An example will make this clear.

If I dissolve 6 grams of anhydrous magnesium sulphate ($MgSO_4=120$), *i.e.*, $\frac{1}{20}$ of a molecular weight, in 100 grams of water, I produce a lowering of the freezing-point of 0°.958. But if we admit that 6.3 grams of the water are united with the dissolved salt to form a hydrate with $7H_2O$ (which appears to me not very probable), the weight of the water acting as solvent is reduced to 93.7 grams. We have, then, for the molecular lowering of the salt:

$$T=\frac{0.958\times120\times93.7}{6\times100}=17.95.$$

If, on the contrary, we suppose that the dissolved salt exists in the anhydrous state, we find:

$$T=\frac{0.958\times120}{6}=19.16.$$

The digression is relatively only $\frac{1}{20}$; and if the first value was correct, this digression would still diminish with the more dilute solutions, until it almost completely disappeared. Another advantage, equally important, which results from using very dilute solutions, is that a sufficient quantity of ice can be produced during the experiment, without greatly changing the concentration of the solution. The result is, the thermometer remains stationary for a long time, usually for several minutes, and the temperature indicated can be determined with the greatest precision.

Without compelling myself to make all of the solutions of the same dilution (which would have unnecessarily increased the difficulties), I have, as far as possible, made their dilution such, that the lowering of the freezing-point should be between 1° and 2°. This lowering is, indeed, quite sufficient, since it can be determined to about $\frac{1}{200}$ of a degree, as I have already explained. (*Ibid.*)

The solvents which I have employed in these researches are:

	FREEZING-POINT.
Water	0°.00
Benzene	4°.96
Nitrobenzene	5°.28
Ethylene bromide	7°.92
Formic acid	8°.52
Acetic acid	16°.75

Since in the experiments on the freezing-point the cooling is *slow*, and since the liquid is constantly agitated, that portion which solidifies appears in the form of glistening plates, or of very small crystalline grains which float in the liquid. It is always the pure solvent which separates, at least at the beginning of the freezing and under the conditions which I employed. The freezing-point can thus be obtained by the process indicated, with a very great degree of accuracy, as well when the solvent is pure as when it contains a substance dissolved in it.

The lowering of the freezing-point due to the presence of a foreign substance in one of these solvents, is always obtained by taking the difference between the freezing-point of the solution and that of the pure solvent, determined in the same way, and with only a short interval between the determinations. If P is the weight of the solvent, P' that of the dissolved substance, and K the lowering of the freezing-point as obtained experimentally, we have for the coefficient of lowering A, (*i. e.*, the lowering produced by 1 gram of the substance in 100 grams of the solvent):

$$A = K\frac{P}{P' \times 100}$$

for all of the solutions of the dilution which I employed, thus following the law of Blagden, at least approximately. The substances to be dissolved are used in as pure condition as possible, and weighed with the usual precautions. If they are volatile they are weighed in bulbs, which are afterwards broken by shaking in the closed flasks containing a known weight of the solvent.

SOLUTIONS IN ACETIC ACID.

Although *acetic acid* undergoes very marked undercooling, it always freezes exactly at the same temperature when in contact

with a portion of the acid previously solidified. The crystals formed, although heavier than the liquid, float in it during the stirring, in the form of glistening plates. A bath of water containing ice suffices to cool the acid, and it must be used in all of the experiments.

Acetic acid can dissolve a large number of substances, particularly those of an organic nature. It is absolutely necessary to use this acid completely dehydrated, *i. e.*, without any water, for those experiments which have to do with hygroscopic substances. But for other substances an acid such as is found in commerce, containing from one to two per cent. of water, can be used without any inconvenience. The compounds to be dissolved in the acid ought always to be dry and freed from water of crystallization. Otherwise the water which they would introduce into the solvent would complicate the results. We can avoid the difficulty of obtaining acetic acid absolutely free from water by making several determinations, after having added to the same liquid, in succession, new quantities of the substance to be investigated. If the substance is very hygroscopic, the quantity first added generally takes up the water dissolved in the acid, and gives a very small lowering. The quantities next added find no more water present, and give a constant lowering. It is the latter which is adopted. The following table contains a summary of my results:

TABLE I.*

Freezing-Point Lowerings of Solutions in Acetic Acid.

SUBSTANCES DISSOLVED IN ACETIC ACID.	FORMULAS.	MOLECULAR LOWERINGS. $T=MA$.
Methyl iodide	CH_3I	38.8
Chloroform	$CHCl_3$	38.6
Carbon tetrachloride	CCl_4	38.9
Carbon bisulphide	CS_2	38.4
Hexane	C_6H_{14}	40.1
Ethylene chloride	$C_2H_4Cl_2$	40.0
Oil of turpentine	$C_{10}H_{16}$	39.2

* The molecular weights, M, and the lowering coefficients, A, are omitted in this and the following tables; their product, T, which is the value of importance, being given.

TABLE I.—(*Continued.*)

SUBSTANCES DISSOLVED IN ACETIC ACID.	FORMULAS.	MOLECULAR LOWERINGS. $T = MA$.
Nitrobenzene	$C_6 H_5 NO_2$	41.0
Naphthalene	$C_{10} H_8$	39.2
Methyl nitrate	$CH_3 NO_3$	38.7
Methyl salicylate	$C_8 H_8 O_3$	39.1
Ether	$C_4 H_{10} O$	39.4
Ethyl sulphide	$C_4 H_{10} S$	38.5
Ethyl cyanide	$C_3 H_5 N$	37.6
Ethyl formate	$C_3 H_6 O_2$	37.2
Ethyl valerate	$C_7 H_{14} O_2$	39.6
Allyl sulphocyanate	$C_4 H_5 NS$	38.2
Aldehyde	$C_2 H_4 O$	38.4
Chloral	$C_2 HO Cl_3$	39.2
Benzaldehyde	$C_7 H_6 O$	39.7
Camphor	$C_{10} H_{16} O$	39.0
Acetone	$C_3 H_6 O$	38.1
Acetic anhydride	$C_4 H_6 O_3$	36.6
Formic acid	$CH_2 O_2$	36.5
Butyric acid	$C_4 H_8 O_2$	37.3
Valeric acid	$C_5 H_{10} O_2$	39.2
Benzoic acid	$C_7 H_6 O_2$	43.0
Camphoric acid	$C_{10} H_{16} O_4$	40.0
Salicylic acid	$C_7 H_6 O_3$	40.5
Picric acid	$C_6 H_3 N_3 O_7$	39.8
Water	$H_2 O$	33.0
Methyl alcohol	$CH_4 O$	35.7
Ethyl alcohol	$C_2 H_6 O$	36.4
Butyl alcohol	$C_4 H_{10} O$	38.7
Amyl alcohol	$C_5 H_{12} O$	39.4
Allyl alcohol	$C_3 H_6 O$	39.1
Glycerin	$C_3 H_8 O_3$	36.2
Salicin	$C_{13} H_{18} O_7$	37.9
Santonin	$C_{15} H_{18} O_3$	38.1
Phenol	$C_6 H_6 O$	36.2
Pyrogallol	$C_6 H_6 O_3$	37.3
Hydrocyanic acid	$H CN$	36.6
Acetamide	$C_2 H_5 NO$	36.1

TABLE I.—(*Concluded.*)

SUBSTANCES DISSOLVED IN ACETIC ACID.	FORMULAS.	MOLECULAR LOWERINGS. $T=MA$.
Ammonium acetate	$C_2 H_7 NO_2$	35.0
Aniline acetate	$C_8 H_{11} NO_2$	36.2
Quinine acetate	$C_{24} H_{32} N_2 O_6$	41.0
Strychnine acetate	$C_{23} H_{26} N_2 O_4$	41.6
Brucine acetate	$C_{25} H_{30} N_2 O_6$	40.0
Codeïne acetate	$C_{20} H_{25} NO_5$	38.3
Morphine acetate	$C_{38} H_{46} N_2 O_{10}$	43.0
Potassium acetate	$C_2 H_3 KO_2$	39.0
Sulphur monochloride	$S_2 Cl_2$	38.7
Arsenic trichloride	$As Cl_3$	41.5
Tin tetrachloride	$Sn Cl_4$	41.3
Hydrogen sulphide	$H_2 S$	35.6
Sulphur dioxide	SO_2	38.5
		ABNORMAL LOWERINGS.
Sulphuric acid	$H_2 SO_4$	18.6
Hydrochloric acid	$H Cl$	17.2
Magnesium acetate	$C_4 H_6 O_4 Mg$	18.2

An examination of the preceding table gives rise to two important remarks :

1. *For substances dissolved in acetic acid there is a maximum molecular lowering, which is* 39. A few substances like benzoic acid and morphine acetate, have, it is true, a lowering as great as 43 ; but everything points to the conclusion that this extraordinary amount of lowering is only apparent, and that it results from some chemical action, such, for example, as the combination of the dissolved substance with some molecules of the solvent.

2. Of the fifty-nine substances in this table, fifty-six have a molecular lowering between 37 and 41, and always close to 39, which I take as the normal lowering. Only three give an abnormal lowering, which is close to 18, and is nearly half the preceding value. These three substances, which appear at the end of the list, are of mineral nature, and it is to be observed that they are very hygroscopic. Thus : *The molecular lowerings*

produced by the different compounds in acetic acid approach two numbers, 39 *and* 18, *of which the one, produced in the great majority of cases, is obviously double the other.*

SOLUTIONS IN FORMIC ACID.

The formic acid which I employed froze at 8°.52, presenting the same phenomena as acetic acid. The solvent power of this acid appears to be just as great as that of acetic acid. It seems to be even greater for the compounds soluble in water. But its high price and the difficulty of obtaining it again from the solutions have prevented me from making very extensive experiments with it. Table II. gives a résumé of the results obtained.

TABLE II.

Freezing-Point Lowerings of Solutions in Formic Acid.

SUBSTANCES DISSOLVED IN FORMIC ACID.	FORMULAS.	MOLECULAR LOWERINGS. $T=MA$.
Chloroform	$CHCl_3$	26.5
Benzene	C_6H_6	29.4
Ether	$C_4H_{10}O$	28.2
Aldehyde	C_2H_4O	26.1
Acetone	C_3H_6O	27.8
Acetic acid	$C_2H_4O_2$	26.5
Brucine formate	$C_{24}H_{28}N_2O_6$	29.7
Potassium formate	$CHKO_2$	28.9
Arsenic trichloride	$AsCl_3$	26.6
		ABNORMAL LOWERING.*
Magnesium formate	C_2HO_4Mg	13.9

The above table gives rise to two remarks already made for acetic acid:

1. *There is a* maximum *of molecular lowering of the freezing-point for substances dissolved in formic acid, which is about* 29.

2. *The molecular lowerings of the freezing-point produced by the different compounds in formic acid approach the two numbers* 28 *and* 14, *the one being twice the other.*

* [*Unimportant note omitted.*]

SOLUTIONS IN BENZENE.

The *benzene* sold under the name of *crystallizable benzene*, and which freezes at about 5°, is nearly chemically pure, and very well adapted for use. The results which it gives do not differ from those obtained with the purest benzene made from benzoic acid. The undercooling which is always produced, as in the preceding liquids, is removed by contact with a particle of solid benzene, and small opaque crystals of benzene are seen to increase in number immediately, which, although more dense than the liquid, float in it during the stirring.

The results obtained are summarized in the following table:

TABLE III.

Freezing-Point Lowerings of Solutions in Benzene.

SUBSTANCES DISSOLVED IN BENZENE.	FORMULAS.	MOLECULAR LOWERINGS. $T=MA$.
Methyl iodide	CH_3I	50.4
Chloroform	$CHCl_3$	51.1
Carbon tetrachloride	CCl_4	51.2
Carbon bisulphide	CS_2	49.7
Ethyl iodide	C_2H_5I	51.6
Ethyl bromide	C_2H_5Br	50.2
Hexane	C_6H_{14}	51.3
Ethylene chloride	$C_2H_4Cl_2$	48.6
Oil of turpentine	$C_{10}H_{16}$	49.8
Nitrobenzene	$C_6H_5NO_2$	48.0
Naphthalene	$C_{10}H_8$	50.0
Anthracene	$C_{14}H_{10}$	51.2
Methyl nitrate	CH_3NO_3	49.3
Methyl oxalate	$C_4H_6O_4$	49.2
Methyl salicylate	$C_8H_8O_3$	51.5
Ether	$C_4H_{10}O$	49.7
Ethyl sulphide	$C_4H_{10}S$	51.8
Ethyl cyanide	C_3H_5N	51.6
Ethyl formate	$C_3H_6O_2$	49.3
Ethyl valerate	$C_7H_{14}O_2$	50.0
Oil of mustard	C_4H_5NS	51.4
Nitroglycerin	$C_3N_3H_5O_9$	49.9

TABLE III.—(*Continued.*)

SUBSTANCES DISSOLVED IN BENZENE.	FORMULAS.	MOLECULAR LOWERINGS. $T=MA$.
Tributyrin	$C_{15}H_{26}O_6$	48.7
Triolein	$C_{57}H_{104}O_6$	49.8
Aldehyde	C_2H_4O	48.7
Chloral	C_2HOCl_3	50.3
Benzaldehyde	C_7H_6O	50.1
Camphor	$C_{10}H_{16}O$	51.4
Acetone	C_3H_6O	49.3
Valerone	$C_9H_{18}O$	51.0
Acetic anhydride	$C_4H_6O_3$	47.0
Santonin	$C_{15}H_{18}O_3$	50.2
Picric acid	$C_6H_3N_3O_7$	49.9
Aniline	C_6H_7N	46.3
Narcotine	$C_{22}H_{23}NO_7$	52.1
Codeïne	$C_{18}H_{21}NO_3$	48.7
Thebaïne	$C_{19}H_{21}NO_3$	48.0
Sulphur monochloride	S_2Cl_2	51.1
Arsenic trichloride	$AsCl_3$	49.6
Phosphorus trichloride	PCl_3	47.2
Phosphorus pentachloride	PCl_5	51.6
Stannic chloride	$SnCl_4$	48.8
		ABNORMAL LOWERINGS.
Methyl alcohol	CH_4O	25.3
Ethyl alcohol	C_2H_6O	28.2
Butyl alcohol	$C_4H_{10}O$	43.2
Amyl alcohol	$C_5H_{12}O$	39.7
Phenol	C_6H_6O	32.4
Formic acid	CH_2O_2	23.2
Acetic acid	$C_2H_4O_2$	25.3
Valeric acid	$C_5H_{10}O_2$	27.1
Benzoic acid	$C_7H_6O_2$	25.4

This table gives rise to the same remarks as the preceding.

1. *For substances dissolved in benzene there is a* maximum *lowering of the freezing-point.* This maximum lowering appears

to be about 50. Some lowerings, it is true, are a little above this figure, but the difference seems to me to be due either to impurities or to some action exerted upon the solvent.

2. For the hydrocarbons and their derivatives, the ethers, aldehydes, acetones, acid anhydrides, glucosides, alcaloids, and chlorides of the metalloids, the molecular lowering of the freezing-point in benzene lies between 48 and 51, and always approaches 49, a number which ought to be considered the mean normal molecular lowering in benzene. As to the alcohols, phenol, and the acids (that is, the compounds which contain hydroxyl), their molecular lowering in benzene generally lies between 23 and 27, and approaches the mean 25, a number which is obviously half the mean of the normal lowering. The only hydroxyl compound which produces the normal lowering in benzene is picric acid; but we know that this acid forms a definite compound with the benzene, thus making it an exceptional substance. Two or three alcohols give an intermediate lowering. We thus see that *in benzene,* as in the preceding solvents, *the molecular lowerings of the freezing-point of the different compounds are grouped around two values,* 49 *and* 25, *the one being, obviously, twice the other.*

It should be observed that the smaller of these two values, which appears, only exceptionally with acetic and formic acids, occurs more frequently when benzene is used as solvent.

SOLUTIONS IN NITROBENZENE.

It is difficult to find commercial nitrobenzene sufficiently pure for these experiments. I prepared the specimen which I used. For this purpose I treated pure benzene with nitric acid, at only a slightly elevated temperature, so as to entirely avoid the production of dinitrobenzene. The product, washed with sodium carbonate and water, was separated by fractional distillation from the excess of benzene and other impurities. The nitrobenzene thus obtained distils completely at 205°, and freezes at 5°.28. Nitrobenzene, like the preceding solvents, undergoes undercooling, and in contact with a solidified particle of the same substance it freezes in the form of small crystals, which, notwithstanding their great density, float in the liquid during the stirring.

The law relating to the molecular lowerings produced by the

different substances in a given solvent being clearly established by the preceding experiments, I limited myself to ascertain whether it is verified with nitrobenzene. I obtained the following results:

TABLE IV.

Freezing-Point Lowerings of Solutions in Nitrobenzene.

SUBSTANCES DISSOLVED IN NITROBENZENE.	FORMULAS.	MOLECULAR LOWERINGS. $T=MA$.
Chloroform	$CHCl_3$	69.9
Carbon bisulphide	CS_2	70.2
Oil of turpentine	$C_{10}H_{16}$	69.8
Benzene	C_6H_6	70.6
Naphthalene	$C_{10}H_8$	73.6
Ether	$C_4H_{10}O$	67.4
Ethyl valerate	$C_7H_{14}O_2$	73.2
Ethyl acetate	$C_4H_8O_2$	72.2
Benzaldehyde	C_7H_6O	70.3
Acetone	C_3H_6O	69.2
Codeïne	$C_{18}H_{21}NO_3$	73.5
Arsenic trichloride	$AsCl_3$	67.5
Stannic chloride	$SnCl_4$	71.4
		ABNORMAL LOWERINGS.
Methyl alcohol	CH_4O	35.4
Ethyl alcohol	C_2H_6O	35.6
Acetic acid	$C_2H_4O_2$	36.1
Valeric acid	$C_5H_{10}O_2$	42.4
Benzoic acid	$C_7H_6O_2$	37.7

We see that the effects produced in nitrobenzene by compounds of the different chemical types, are exactly analogous to those which the same substances produce in benzene. *There is a* maximum *of the molecular lowering, which appears to be close to* 73, *for the substances which do not act chemically upon the solvent.*

The hydrocarbons and their substitution products, the ethers, aldehydes, and acetones, and the chlorides of the metalloids, produce in nitrobenzene lowerings which always lie between 67 and 73, in general about 72.

The alcohols and the acids (*i. e.*, the hydroxyl compounds) give molecular lowerings in nitrobenzene between 35.5 and 42.2, and generally about 36, which is equal to half the preceding number.

SOLUTIONS IN ETHYLENE BROMIDE.

The ethylene bromide which I used froze at 7°.92, giving crystalline opaque plates heavier than the liquid. Like all the other solvents which can be frozen, it always undergoes undercooling, but to a less extent. Its solvent power is, as it appeared to me, exactly analogous to that of benzene and chloroform. It undergoes a slow change, which in two or three days lowers its freezing-point to an appreciable extent. The solutions ought, therefore, to be always made just before they are used. I limited myself to proving by some experiments that the laws observed in the preceding cases are applicable here. The following results were obtained:

TABLE V.

SUBSTANCES DISSOLVED IN ETHYLENE BROMIDE.	FORMULAS.	MOLECULAR LOWERINGS. $T=MA$.
Carbon bisulphide	CS_2	116.6
Chloroform	$CHCl_3$	118.4
Benzene	C_6H_6	119.2
Ether	$C_4H_{10}O$	117.5
Arsenic trichloride	$AsCl_3$	118.1
		ABNORMAL LOWERINGS.
Acetic acid	$C_2H_4O_2$	57.7
Alcohol	C_2H_6O	56.8

Therefore:

1. *There is a* maximum *of molecular lowering in ethylene bromide, which is approximately* 119.

2. *The molecular lowerings produced by different compounds in this solvent, approach the two values* 118 *and* 58, *the one being double the other;* a result similar to those which we have observed with all the preceding solvents.

AQUEOUS SOLUTIONS.

As I have observed elsewhere, water is the only solvent which was employed by my predecessors, and the metallic salts the only substances which were dissolved in it. The results obtained, although numerous and remarkable, especially from the point of view of the existence of saline hydrates in the solutions, do not admit of general conclusions. It is right to recall, however, that De Coppet has recognized that *the salts of the same chemical constitution have nearly the same molecular lowering;* an important result which is the first clew to the great law to which the phenomenon conforms. (*Ann. Chim. Phys.*, [4], **25**.) After this remark De Coppet divided salts into five groups, as follows, having nearly the same molecular lowering:

	MOLECULAR LOWERINGS.
(1) Chlorides and hydrates of potassium and sodium.	34
(2) Chlorides of barium and of strontium.....	45
(3) Nitrates of potassium, sodium, and ammonium...	27
(4) Chromate, sulphate, carbonate of potassium; sulphate of ammonium.....	38
(5) Sulphates of zinc, magnesium, iron, copper.....	17

The results pertaining to salts in aqueous solution present, therefore, a peculiar complication, which we have not met with in the other solvents. However, the lowerings produced in water appear discordant only when they are examined closely and separately. As soon as we consider all of the effects produced, not only by the salts (which behave in a very special manner), but also by the soluble oxides, by the mineral acids, and especially by the organic substances, we recognize also here the manifestation of the general law. This will be seen from the following table. I have not introduced the salts of the metals whose atomicity is greater than 2, because they all appear to undergo more or less decomposition in water:

TABLE VI.

Lowering of the Freezing-Point of Aqueous Solutions.

SUBSTANCES DISSOLVED IN WATER.	FORMULAS.	MOLECULAR LOWERINGS. $T=MA$.
Hydrochloric acid	HCl	39.1
Hydrobromic acid	HBr	39.6
Nitric acid	HNO_3	35.8
Perchloric acid	$HClO_4$	38.7
Arsenic acid (?)	H_3AsO_4	42.6
Phosphoric acid	H_3PO_4	42.9
Sulphuric acid	H_2SO_4	38.2
Selenious acid	SeO_2	42.9
Hydrofluosilicic acid	H_2SiF_6	46.6
Potassium hydrate	KOH	35.3
Sodium hydrate	$NaOH$	36.2
Lithium hydrate	$LiOH$	37.4
Potassium chloride	KCl	33.6
Sodium chloride	$NaCl$	35.1
Lithium chloride	$LiCl$	36.8
Ammonium chloride	NH_4Cl	34.8
Potassium iodide	KI	35.2
Potassium bromide	KBr	35.1
Potassium cyanide	KCN	32.2
Potassium ferrocyanide	$K_4Fe(CN)_6$	46.3
Potassium ferricyanide	$K_3Fe(CN)_6$	47.3
Sodium nitroprussiate	$NaFe(CN)_5NO$	46.8
Potassium sulphocyanate	$KCNS$	33.2
Potassium nitrate	KNO_3	30.8
Sodium nitrate	$NaNO_3$	34.0
Ammonium nitrate	NH_4NO_3	32.0
Potassium formate	$KCHO_2$	35.2
Potassium acetate	$KC_2H_3O_2$	34.5
Sodium acetate	$NaC_2H_3O_2$	32.0
Potassium carbonate	K_2CO_3	41.8
Sodium carbonate	Na_2CO_3	40.3
Potassium sulphate	K_2SO_4	39.0
Acid potassium sulphate	$KHSO_4$	34.8
Sodium sulphate	Na_2SO_4	35.4
Ammonium sulphate	$(NH_4)_2SO_4$	37.0

TABLE VI.—(*Continued.*)

SUBSTANCES DISSOLVED IN WATER.	FORMULAS.	MOLECULAR LOWERINGS. $T=MA$.
Sodium tetraborate (borax)	$Na_2 B_4 O_7$	66.0
Potassium chromate.....	$K_2 Cr O_4$	38.1
Potassium bichromate.....	$K_2 Cr_2 O_7$	43.7
Disodium phosphate	$Na_2 H P O_4$	37.9
Sodium pyrophosphate	$Na_4 P_2 O_7$	45.8
Potassium oxalate.....	$K_2 C_2 O_4$	46.8
Sodium oxalate.....	$Na_2 C_2 O_4$	43.2
Potassium tartrate.....	$K_2 C_4 H_4 O_6$	36.3
Sodium tartrate.....	$Na_2 C_4 H_4 O_6$	44.2
Acid sodium tartrate.....	$NaH C_4 H_4 O_6$	31.2
Barium hydroxide.....	$Ba(OH)_2$	49.7
Strontium hydroxide.....	$Sr(OH)_2$	48.2
Calcium hydroxide.....	$Ca(OH)_2$	48.0
Barium chloride.....	$Ba Cl_2$	48.6
Strontium chloride.....	$Sr Cl_2$	51.1
Calcium chloride.....	$Ca Cl_2$	49.9
Cupric chloride.....	$Cu Cl_2$	47.8
Barium nitrate.....	$Ba(NO_3)_2$	40.5
Strontium nitrate.....	$Sr(NO_3)_2$	41.2
Calcium nitrate.....	$Ca(NO_3)_2$	37.4
Lead nitrate.....	$Pb(NO_3)_2$	37.4
Barium formate.....	$Ba C_2 H_2 O_4$	48.2
Barium acetate.....	$Ba C_4 H_6 O_4$	48.6
Magnesium acetate.....	$Mg C_4 H_6 O_4$	47.8
		ABNORMAL LOWERINGS.
Sulphurous acid.....	SO_2	20.0
Hydrogen sulphide.....	$H_2 S$	19.2
Arsenious acid.....	$H_3 As O_3$	20.3
Metaphosphoric (?) acid	$H P O_3$	21.7
Boric acid.....	$H_3 B O_3$	20.5
Potassium antimonyl tartrate...	$K Sb C_4 H_4 O_7$	18.4
Mercuric cyanide.....	$Hg(CN)_2$	17.5
Magnesium sulphate.....	$Mg SO_4$	19.2
Ferrous sulphate.....	$Fe SO_4$	18.4
Zinc sulphate.....	$Zn SO_4$	18.2
Copper sulphate.....	$Cu SO_4$	18.0

TABLE VI.—(*Concluded.*)

*Organic Compounds.**

SUBSTANCES DISSOLVED IN WATER.	FORMULAS.	ABNORMAL LOWERINGS. $T = MA$.
Methyl alcohol	CH_4O	17.3
Ethyl alcohol	C_2H_6O	17.3
Butyl alcohol	$C_4H_{10}O$	17.2
Glycerin	$C_3H_8O_3$	17.1
Mannite	$C_6H_{14}O_6$	18.0
Dextrose	$C_6H_{12}O_6$	19.3
Milk sugar	$C_{12}H_{22}O_{11}$	18.1
Salicin	$C_{13}H_{18}O_7$	17.2
Phenol	C_6H_6O	15.5
Pyrogallol	$C_6H_6O_3$	16.3
Chloral hydrate	$C_2Cl_3H_3O_2$	18.9
Acetone	C_3H_6O	17.1
Formic acid	H_2CO_2	19.3
Acetic acid	$C_2H_4O_2$	19.0
Butyric acid	$C_4H_8O_2$	18.7
Oxalic acid	C_2H_2O	22.9
Lactic acid	$C_3H_6O_3$	19.2
Malic acid	$C_4H_6O_5$	18.7
Tartaric acid	$C_4H_6O_6$	19.5
Citric acid	$C_6H_8O_7$	19.3
Ether	$C_4H_{10}O$	16.6
Ethyl acetate	$C_4H_8O_2$	17.8
Hydrocyanic acid	HCN	19.4
Acetamide	C_2H_5NO	17.8
Urea	CON_2H_4	17.2
Ammonia	NH_3	19.9
Ethylamine	C_2NH_7	18.5
Propylamine	C_3NH_9	18.4
Aniline	C_6NH_7	15.3

Notwithstanding the variations which are much larger than with the other solvents, we find here also the laws previously observed.

* [*This table is taken from Ann. Chim. Phys.*, (5), **28**, 137 (1883).]

For the compounds which are not dissociated in water there is a maximum *of the molecular lowering, which is about* 47.*

The molecular lowerings of some salts which are not decomposable by water are, it is true, larger than this value. But this arises, in a great measure, from the fact that they are referred to substances which we suppose to be anhydrous, while these really exist as hydrates in the solutions. As an example, the molecular lowering of barium chloride is 48.6 when we suppose this salt to be anhydrous in the solutions, but falls to 46.9 when we suppose it to exist in the solutions as the hydrate $Ba\ Cl_2+2\ H_2\ O$, as Rüdorff thinks it does. Some deviations ought also to be attributed to impurities.

Two compounds are exceptions to this law, if we adopt for them molecular weights which are double the equivalents, as most modern chemists are inclined to do. These are : potassium ferricyanide and sodium nitroprussiate. As a matter of fact, with the formulas $K_6 Fe_2 (CN)_{12}$ and $Na_4 (NO)_2 Fe_2 (CN)_{10}$ we find for the molecular lowering of each of these substances a value which is exactly double the *maximum*, 47. But these formulas do not appear to be necessary for the explanation of the chemical properties of these substances, and nothing is opposed, as far as I know, to assigning to them, at least in solution, the formulas $K_3\ Fe\ (CN)_6$ and $Na_2\ NO\text{-}Fe\ (CN)_5$, which correspond to the maximum molecular lowering. The only serious objection resulting from the formula $K_3\ Fe\ (CN)_6$ is that potassium ferricyanide appears to be a substance containing an odd number of unsaturated bonds. But this anomaly is found in some other compounds—*e. g.*, in aluminium ethyl—and it alone is not a sufficient reason for condemning a formula which agrees so well with the physical facts. I have, therefore, adopted for these substances molecular weights equal to the equivalents.

A glance at the figures in the last column of the preceding table shows that *the molecular lowerings of the freezing-point of water are grouped around the two numbers* 37 *and* 18.5, *the one being double the other;* so that the law observed with acetic

* Borax, which decomposes in water, as Berthelot has shown (*Méchan. Chim.*, II., 224), appears in the table with a molecular lowering of 66. But this number is, in reality, the sum of the molecular lowerings of the acid and base into which the original salt decomposes, and each of these appears in the law enunciated.

acid, formic acid, benzene, nitrobenzene, and ethylene bromide, still manifests itself, although less clearly, when water is used as a solvent.

One fact shows clearly the simple relation which exists, even in water, between the normal and abnormal lowerings. The solution of anhydrous phosphoric acid in water, made in the cold, has, for more than an hour, a molecular lowering of 21.7. If it is boiled and the liquid brought to the original volume by adding water, we find that the molecular lowering is about 44.2, that is, it is doubled.

The molecular lowerings of all the salts of the alkalies and alkaline earths, of all the strong acids and bases, are grouped around the mean normal lowering 37. The abnormal molecular lowering 18.5 belongs to some salts of the bivalent metals, to all the weak acids and bases, and, without exception, to all of the organic compounds which are non-saline.

CONCLUSIONS.

Several important propositions follow from the mass of facts recorded in this paper:

1. *Every substance, solid, liquid, or gaseous, when dissolved in a definite liquid compound capable of solidifying, lowers its freezing-point.* This fact, which it was impossible to foresee, and of which it will be very interesting to know the cause, is absolutely general. The exceptions which are observed are only apparent and are easily explained. Thus, when we dissolve anhydrous stannic chloride in acetic acid containing a little water, each molecule of the chloride combines with two molecules of water forming only one molecule of the hydrate. Instead of two molecules in solution, there is, therefore, only one, and an elevation of the freezing-point necessarily results; for, as we shall see later, the amount of lowering depends only upon the relation between the number of molecules of the dissolved substance and of the solvent.

But such an effect is due entirely to the reciprocal action of the dissolved substances. It is never produced when the solvent is a definite compound, free from impurities. It results from the above principle that: *of two specimens of a substance, that one is purer which solidifies or melts at the higher temperature.*

This furnishes an excellent means, unfortunately limited in its applicability, of examining the purity of substances.

2. *There is in each solvent a maximum molecular lowering of the freezing-point.* This maximum lowering is about 47 in water, 36 in acetic acid, 29 in formic acid, 50 in benzene, 73 in nitrobenzene, 119 in ethylene bromide.

This fact can be applied directly to the determination of a certain number of molecular weights. Given a compound whose molecular weight it is desired to know; we determine its coefficient of lowering, A, in one of the preceding solvents, then divide the *maximum* molecular lowering of the solvent employed by A, and we obtain the *maximum* of the molecular weight. We know, besides, that the molecular weight corresponds to the simplest atomic formula of the compound examined, or to a whole multiple of this formula. Whenever, then, the *maximum* found is not twice the molecular weight corresponding to the simplest atomic formula, the latter ought to be adopted.

3. *The molecular lowerings of the freezing-point of all the solvents, produced by the different compounds dissolved in them, approach two mean values, which vary with the nature of the solvent, the one being twice the other.* These mean values are 117 and 58 for ethylene bromide, 72 and 36 for nitrobenzene, 49 and 24 for benzene, 39 and 19 for acetic acid, 28 and 14 for formic acid, 37 and 18.5 for water. The larger of the two lowerings, which I call *normal lowering*, is produced much more frequently than the smaller, and in all the solvents studied, with the exception of water, it is obviously identical with the maximum molecular lowering. In formic and acetic acids it appears almost constantly. In benzene, nitrobenzene, and ethylene bromide, it is produced by all substances which do not contain hydroxyl, and consequently by all substances which have a constitution analogous to that of the solvents. In water it is produced by the strong acids, and by the salts whose acid or base is monatomic.

The substances which produce normal or abnormal lowering in a given solvent belong to well-defined groups, and this fact can also be utilized for the determination of MOLECULAR WEIGHTS. All the salts of the alkalies in solution in water give a molecular lowering which is approximately 37. If, then, we have to choose between several numbers which are multiples

of one another, for the molecular weight of a salt of an alkali, we choose that one which, multiplied by the coefficient of lowering of the salt in water, gives the number nearest to 37. Similarly, with respect to the organic substances soluble in water, that molecular weight is to be adopted which, multiplied by the coefficient of lowering in water, gives the number nearest to 18.5 (*Ann. Chim. Phys.*, January, 1883). All organic substances in solution in acetic acid give a molecular lowering of about 39. The formula which must be adopted for an organic compound soluble in this solvent is, then, that which corresponds to the molecular weight the closest to the number obtained by dividing 39 by the coefficient of lowering of this substance in acetic acid. As most of the compounds are soluble either in water or in acetic acid, this method furnishes the means of establishing the molecular weights in a large number of cases. If necessary, the coefficients of lowering in benzene, or in other solvents, can be turned to account. There are, then, but few compounds, whatever their nature, whose molecular weight cannot be established by the method of freezing the solvents. But I must not enlarge further upon this subject here, and shall return to it in a special work. It suffices to have indicated this important application.

Returning to the experimental facts already stated, we can explain them by admitting that: *In a constant weight of a given solvent, all the physical molecules, whatever their nature, produce the same lowering of the freezing-point.* According to this hypothesis, when the dissolved substances are completely disintegrated, as they would be in a perfect vapor, and when each physical molecule contains only one chemical molecule, the molecular lowering is a *maximum*, and the same for all. When the chemical molecules are united in pairs, to a greater or less extent, forming a certain number of double physical molecules, the lowering produced is less than if the condensation had not taken place, since each of these double molecules produces the same effect as one simple molecule. If all of the chemical molecules are united in pairs, the lowering is half the *maximum*. The abnormal lowerings in almost all of the solvents correspond to this condition. When water is employed as solvent, we observe a certain number of abnormal lowerings, which are considerably less than half the maximum lowering. This shows that the condensation can proceed still further. The exceptionally small

lowering of phenol and pyrogollol in water can be explained by assuming that the molecules of these substances are united in groups of three. To explain all of the facts observed, it therefore suffices to apply to the constitution of dissolved substances the hypotheses admitted by all for the constitution of vapors.

The preceding considerations explain the effects produced by different compounds in a given solvent; but they indicate nothing as to the value of the lowering produced by a given compound in different solvents.

In order to bring out the law relating to the nature of the solvents, it is necessary to reduce the results by calculation to the case of 1 molecule of each substance dissolved in 100 molecules of the solvent. This is accomplished by dividing the molecular lowering of each substance, T, by the molecular weight of the solvent, M'. Indeed, the molecular lowerings are those produced by 1 molecule of a foreign substance in 100 grams, or in $\frac{100}{M'}$ molecules of the solvent. Moreover, from the law of Blagden, the lowerings are, *ceteris paribus*, inversely proportional to the quantities of solvent which contain 1 molecule dissolved in them. We have then, calling T' the lowering produced by 1 molecule dissolved in 100 molecules:

$$T \times \frac{100}{M'} = T' \times 100,$$

from which:

$$T' = \frac{T}{M'}.$$

If, then, we divide the molecular lowerings indicated above by the molecular weights of the solvents to which they refer, we reduce the results to the case of 1 molecule of the dissolved substance in 100 molecules of the solvent. Below are the results obtained by introducing into the calculation the values of T corresponding to a *maximum* molecular lowering:

Solvents.	Molecular Weights of Solvents.	Maximum Molecular Lowering Produced by 1 Molecule in 100 Grams.	Maximum Molecular Lowering Divided by the Molecular Weight of the Solvent, or Lowering Produced by 1 Molecule in 100 Molecules.
Water.....	18	47	2°.61
Formic acid.....	46	29	0°.63
Acetic acid.....	60	39	0°.65
Benzene.....	78	50	0°.64
Nitrobenzene....	123	73	0°.59
Ethylene bromide	188	119	0°.63

Leaving out of the question for the moment water, which behaves in a peculiar manner, we see that the *maximum* lowering of the freezing-point, which results from the action of 1 molecule dissolved in 100 molecules of solvents, varies only from 0°.59 to 0°.65, mean 0°.63, and is consequently nearly the same in all of the solvents. This fact is the more remarkable since the molecular lowerings which enter into the calculation vary considerably—namely, in the ratio of 1 to 4. It is, moreover, reasonable. In fact, whatever is the nature of the action exerted between the molecules of the solvent and those of the dissolved substance, it seems that it ought to be mutual; and if the effect is independent of the nature of the dissolved substance, it ought probably to be independent also of the nature of the solvent.

Water is the only exception; but it is not astonishing on the part of a liquid which presents so many other peculiarities. To explain the anomaly, it is allowable to suppose that each of the physical molecules of which water is composed, is formed of several chemical molecules united with one another. At the time when I had found only a few molecular lowerings in aqueous solutions larger than the mean lowering 37, I believed that the physical molecules of water were formed of 3 chemical molecules. Indeed, by dividing 37 by 18×3, we obtain 0.685, which is not very far removed from the mean value 0.63 obtained with other solvents. This I have observed in a previous publication (*Compt. rend.*, November 27th, 1882). But, in the light of new determinations, it is no longer possible to consider as doubtful the molecular lowerings which are much larger than 37, and I am compelled to recognize that the molecular lowerings in water can be even as great as 47, a maximum value in most cases where the dissolved substances do not decompose. Such a lowering can be explained *by admitting that the molecules of water are united in groups of four*, at least in the neighborhood of zero. Then, indeed, 47 divided by 18×4 is 0.65, which is remarkably near the mean 0.63 obtained with other solvents.

The anomalies relating to solvents, like those relating to dissolved substances, can then be explained by the condensation of the molecules, and they do not prevent us from expressing the GENERAL LAW OF THE FREEZING OF SOLVENTS, as follows:

If 1 *molecule of any substance is dissolved in* 100 *molecules of*

any liquid of a different nature, the lowering of the freezing-point of this liquid is always nearly the same, and approximately 0°.63.

Consequently, the lowering of the freezing-point of a dilute solution of any strength whatever is, obviously, equal to the product obtained by multiplying 63 *by the ratio between the number of molecules of the dissolved substance and that of the solvent.*

Let us recall, in conclusion, that the molecules with which we are here dealing are physical molecules, which, in certain cases, can be formed by two or several chemical molecules united with one another.

ON THE VAPOR-PRESSURE OF ETHEREAL SOLUTIONS

BY

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(*Annales de Chimie et de Physique*, [6], **15**, 375, 1888)

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ON THE VAPOR-PRESSURE OF ETHEREAL SOLUTIONS*

BY

F. M. RAOULT

I DISCOVERED some time ago (*Compt. rend.*, July 22, 1878) that a close relation exists between the lowering of the vapor-pressures of aqueous solutions, the lowering of their freezing-points, and the molecular weights of the dissolved substances. This observation was the starting-point for my researches on the freezing-point of solutions (*Compt. rend.*, **94** to **101**), and it is this which now leads me to undertake a similar piece of work on their vapor-pressures.

I employed, first, ethereal solutions, since they lend themselves easily to this kind of study. To simplify the question I shall consider here only the case where the vapor-pressure of the dissolved substances is very small, and is negligible with respect to that of the ether. In a subsequent investigation I shall examine the more general case, where the dissolved substances themselves have a considerable vapor-pressure.

I determined the vapor-pressures of these kinds of solutions by the method of Dalton. I measured with the cathetometer the heights to which the mercury is raised in the barometric tubes, the one containing only mercury, the other, in addition, a small quantity either of pure ether or of ether in which were dissolved different substances which are nearly non-volatile. Before making the measurements I shook all of the solutions, moistening well the walls, and not until ten minutes later did I proceed with the measurements, the temperature remaining constant. In the calculation of the results I have taken care to add to the pressure of the mercury in each tube the pressure

* *Ann. Chim. Phys.*, [6], **15**, 375 (1888); *Ztschr. Phys. Chem.*, **2**, 353 (1888).

which arises from the small column of ether, or of ethereal solution, which is placed upon it. I have even taken the precaution to correct the concentration of the solutions for the small quantity of ether separated as vapor.

The quantities upon which all of the comparisons are based, and which are to be determined, are: the vapor-pressure of the pure ether, f, and the vapor-pressure of the ether containing the dissolved substance, f', the temperature remaining the same. To determine these quantities as accurately as possible, I worked as follows:

Preparation of the Ether.—Pure commercial ether was taken, and after washing it with water it was shaken several times with a concentrated aqueous solution of caustic potash. It was digested over calcium chloride and distilled in a Le Bel and Henninger apparatus with eight bulbs. The portion which distils at a constant temperature was left in contact with thin fragments of sodium for forty-eight hours, in a balloon flask provided with a condenser with eight bulbs. It was then distilled a second time. Nearly all of it distilled at 34°.7 under 760 millimetres pressure. Regnault gave 34°.97 as the boiling-point of ether.

Regnault says that he had considerable trouble in obtaining an ether which was always exactly the same. He observed this substance undergo change by prolonged boiling under slight pressure. He observed it undergo change even at the ordinary temperature, in a flask hermetically closed and freed from air. The change was manifested only by a change in the vapor-pressure (*Mém. de l'Acad. des Sciences*, **26**, 1862). Perhaps this change resulted from the fact that the ether used by Regnault, which had not been distilled from sodium, contained traces of water or of ethyl peroxide. Lieben (*Ann. Chem. Pharm.*, **165**) was not able to prove the presence of any trace of alcohol, even after a year, in ether distilled from sodium and preserved in a closed vessel. For my part, I found that pure ether, preserved for five months in a barometric tube at ordinary temperatures, had, at 15°, exactly the same vapor-pressure as at the beginning. It is not certain but that ether, even when very pure, undergoes a more or less rapid change in the flasks in which it is preserved, and into which the air always penetrates a little. This lowers its vapor-pressure and gives it the property of soiling mercury. It is, therefore, necessary to

use it immediately after it has been distilled from sodium. I have always done this. I do not, however, think that the ether which I employed was absolutely pure. It contained, indeed, a small quantity of a gas which appeared to me to be a hydrocarbon, and from which I never succeeded in completely freeing it. This compelled me to employ very long tubes, as will be seen later.

Preparation of the Solutions.—The substances which I dissolved in ether were chosen from those whose boiling-points are above 160°, and their vapor-pressure at the ordinary temperature was scarcely 6 millimetres of mercury. It is therefore a simple matter to work with them. To make solutions of known strength, a certain quantity of the substance is weighed in flasks of 20 centimetres capacity, provided with good corks. A sufficient quantity of ether is then poured into each of these flasks, which are now closed and reweighed. The increase in weight is the weight of the ether. In preparing dilute solutions—*i. e.*, solutions containing only a small quantity of non-volatile substance—this is weighed in thin-walled bulbs, which are afterwards broken by shaking in the flasks containing a known quantity of ether, which is large with respect to the amount of substance.

Choice of Barometric Tubes.—I employ tubes of colorless glass, and of about 1 centimetre internal diameter. The capillary effect in such tubes is not zero, but we endeavor to make it constant throughout the entire length of the tube by choosing the tubes as nearly cylindrical as possible. This does not prevent the determination of its exact value and correcting the results accordingly, as we will see later. After having cleansed and dried the interior of the tubes, they are drawn out at 90 centimetres from the end to a long tube, which is bent about the middle in the form of a hook. An elliptic ring of not very stout platinum wire is shoved clear up to the top of each of these, and remains there by virtue of its elasticity. This is used to stir the interior liquid.

Filling the Tubes.—To fill one of these tubes it is thrust into a deep mercury bath, the drawn-out end being kept above the bath. When it is almost entirely immersed in the mercury, the descending limb of the bent tube is inserted in a small flask containing the ethereal solution which it is desired to introduce into the tube. The tube and flask are carefully raised and the

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solution is quickly drawn into the tube. When this liquid has reached a depth of about 3 centimetres in the cylindrical portion of the tube, the flask is removed, and without raising the tube farther the point is closed with a burner a few millimetres from the ethereal solution. It is now necessary to expel the gases adhering to the walls, or dissolved in the liquid, without losing any trace of ether by evaporation.

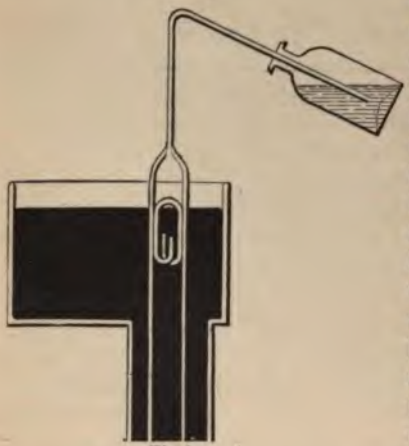

Fig. 1

To accomplish this the barometric tube is raised nearly out of the deep bath, leaving the end only 1 to 2 centimetres under the mercury. By means of two hot irons placed against the tube the solution is boiled with sufficient rapidity, and long enough to drive the mercury down to the bottom. The heating is then discontinued, and the tube again thrust into the deep bath. When the mercury in the interior is on the same plane as that on the exterior, the end of the fine point is cut off with scissors, and then the tube is slowly thrust farther into the bath. The ethereal solution enters the capillary portion, and, when it is only a few millimetres from the end, this is closed with a blow-pipe. The same operation is begun again, then a third time, when there remains in the tube only a trace of gas, which, under atmospheric pressure, generally occupies not more than 3 to 4 millimetres. The influence which this small quantity of gas exerts on the heights of the mercurial columns is negligible in my experiments. Finally, the tube thus prepared was removed to a special mercury bath, wide, and shallow, where it could be observed.

Arrangement for Stirring the Contents of the Tubes.—In the barometric tubes thus prepared, the ethereal solutions, and ether itself if not absolutely pure, tend constantly to lose their homogeneity, due to changes in temperature and to the atmospheric pressure. If the volume of the vapor diminishes,

due to these variations, a certain quantity of ether vapor condenses in each tube, which results in a dilution of the upper portions of the liquid layers in contact with the vapor. The opposite effect is produced if the volume of the vapor increases. If, therefore, care is not taken, the vapor-pressures observed correspond to solutions whose concentration is uncertain, and more or less different from that of the original liquids. To avoid this source of error, not pointed out up to the present, I have always been careful to shake the liquids several minutes before determining their vapor-pressure. At first I seized each tube in succession with wooden forceps, and inclined it until the ether came in contact with the top. I then righted it again, and repeated this several times. I use now the following arrangement, which gives the same result more rapidly and more conveniently:

The mercury bath, in which the barometric tubes rest, is of cast-iron, wide and shallow, and firmly supported on a column of masonry. On its upper edge is a screw-nut in which a screw 10 centimetres long is held vertically, its lower point just touching the surface of the mercury. The barometric tubes, generally six in number, rest upright on a narrow shelf immersed in the mercury of the bath, and which forms the lower part of an iron frame, to which they are fastened by iron wire. The frame can rock with all the tubes which it carries, turning on its base as a hinge, without the end of the tubes coming out of the bath. We are thus able, by inclining the frame and righting it several times, to shake, simultaneously, the solutions contained in all the tubes which it carries, and to wet the walls quite up to the top. The small rings of platinum wire, which are placed up in the top of the tubes, facilitate the stirring very much. The tubes, having been restored to the vertical position, are left to rest for about ten minutes, when the heights are measured.

The necessity of agitation can be easily demonstrated by experiment. Two tubes, the one containing pure ether, the other an ethereal solution, having been placed side by side, are not disturbed for a day or two. The difference between the heights of the mercurial columns is then measured. The tubes are then shaken, and fifteen minutes after the shaking we almost always find considerable increase in this difference, even when the temperature has remained absolutely the same. The increase in the difference is sometimes $\frac{1}{20}$.

On the other hand, I have convinced myself many times that the difference of vapor-pressure in two given tubes is exactly the same at the same temperature, provided the measurement is made after agitation and in the manner just described.

Regulation of the Temperature.—We always work at the temperature of the laboratory, but this is so arranged that the temperature can vary between certain limits or remain almost completely stationary. The laboratory is small, is on the north side, and the sun never shines into it. It is heated by a gas-stove, provided with a thermo-regulator whose reservoir contains 50 litres of air. The air of the laboratory is constantly stirred by the swinging of the door of a closet, which acts as a fan. Thermometers placed to the right, and left, above, and below the barometric tubes constantly indicate the same temperature, and this often remains constant for hours to nearly $\frac{1}{10}$ of a degree.

Measurement of the Heights of the Mercurial Columns.—The heights of the mercury in the different tubes are measured by means of an excellent cathetometer, of 1.50 millimetres range, giving fiftieths of a millimetre. This instrument rests firmly on a column of masonry covered with an iron plate. The tubes to be observed are placed between the cathetometer and a well-lighted glass door, so that the tops of the mercury columns stand out clearly in black against a light background. The end of the screw in contact with the mercury in the bath can be as easily seen, and we are able without difficulty to determine the vertical distance between the upper point of this screw and the level of the mercury in each tube. A normal barometer placed in the same room gives the atmospheric pressure.

Method of Observation.—We choose a moment for the observation when the temperature and atmospheric pressure are as constant as possible. The tubes containing the solutions are shaken, and after ten minutes the observations are begun. The temperature never being exactly constant, the levels are never absolutely stationary. Notwithstanding all this, to obtain very accurate results, recourse is had to the method of alternate observations. Two tubes are observed alternately from minute to minute, the one containing pure ether, the other an ethereal solution, until the heights in two successive observations do not differ more than 0.2 millimetre. If the heights found, in three

consecutive observations on each tube, are in arithmetical progression, the observations are regarded as satisfactory, and the mean of them is taken. A single observation, made at the end, gives the height of the mercury in the tube containing the pure ether. Another gives the height of the barometer.

These quantities being determined, it only remains to know the depressions of the mercury due to capillary action, and to the weight of the liquid added, in order to calculate the vapor-pressures, f and f', of pure ether, and of the solution under consideration.

Correction for the Depression of the Mercury Due to the Liquid Placed Above It and to Capillarity. — After having made all the observations desired on a tube, it is transferred to a deep bath whose upper walls are of glass. It is lowered to $\frac{9}{10}$ its length, and held in this position by means of a stand and clamp. Finally, the slender drawn-out end is cut. The air enters the tube and the mercury within descends below the level in the bath. Enough water is then carefully poured on the mercury of the bath to bring the top of the column of mercury in the tube exactly to the same plane as the mercury in the bath. The height of water added is a measure of the sum of the pressures, due to the weight of liquid placed over the mercury, and to capillarity. It is easy to estimate it in terms of height of mercury column.

Let H be the height of the barometer, h the height of the mercury in the tube containing pure ether, and a the column of mercury equivalent to the weight of liquid placed above it, and to capillarity; h' and a' the corresponding quantities for the tube containing the ethereal solution; δ the difference between the heights of mercury in the two tubes, so that $\delta = h' - h$, all the heights being reduced to zero.

We have, for the vapor-pressure of pure ether, f:

$$f = \mathrm{H} - h - a;$$

and for the vapor-pressure of the ethereal solution examined, f':

$$f' = \mathrm{H} - h - \delta - a'.$$

Error Produced by the Gaseous Residue.—I have stated that ether purified as was indicated contains a small quantity of gas in solution, from which it is very difficult to free it completely. To eliminate as much as possible the influence of this trace of gas on the heights of the mercurial columns, I have found

nothing better than to allow the vapor formed to occupy a large volume. This is the reason why I employ very long tubes, in which the vapor formed occupies always a volume of at least 20 centimetres. Even under these conditions the influence of the gaseous residue is not zero. If, for example, this residue occupies a volume of 5 cubic millimetres under atmospheric pressure, it will produce a pressure of 0.19 millimetre in a volume of 20 centimetres; and the resulting error in the measurement of vapor-pressure is nearly $\frac{2}{10}$ of a millimetre, which is still appreciable. However, as all of the tubes are prepared in the same manner, and since they contain nearly equal quantities of the same ether, the volume of the gaseous residue is everywhere nearly the same. The influence exerted by this residue on the heights of the mercurial columns, therefore, disappears for the most part in the differences, or even in the ratios.

Error Arising from the Solutions Becoming More Concentrated, Due to the Formation of Vapor.—The weight of ether which separates from the solution as vapor, to saturate the relatively large empty space presented to it, is often sufficient to appreciably change the concentration. But it is possible to calculate the amount with sufficient accuracy, and, notwithstanding this, to know the true concentration of the solution in contact with the vapor.

If we represent by n and n' the weights of non-volatile substance dissolved in 100 grams of ether, before and after the production of vapor, we have:

$$\frac{n}{n'}=1-\frac{ldf'\ (100+n)\ 1.3}{l'd'\ (1+at)\ 76\,000\,000},$$

in which l is the length in centimetres which the ether-vapor occupies in the tube; l', the length occupied by the solution; d, the density of ether-vapor referred to air ($d=2.57$); d', the density of the solution; f', the elastic force of the vapor of the solution; t, the temperature; $a=0.00367$.

In the exact calculations n' ought to be substituted for n; but if the temperature is not high, and if the solutions are dilute, the correction is reduced to a mere trifle.

If, for example, we have approximately:

$$n=15,\ l=30,\ f'=300,\ t=16°,\ l'=3,\ d'=0.80,$$

it becomes:

$$n'=1.01+n.$$

That is, the formation of the vapor in this case increases the concentration about $\frac{1}{100}$. The correction would be greater if the temperature were higher and the solution more concentrated. I estimate that, all corrections made, the vapor-pressures, f and f', of the ether and of the ethereal solution, can be obtained to 0.2 of a millimetre.

Influence of Concentration on the Vapor-Pressure of Ethereal Solutions.—I could have wished, for the sake of greater simplicity, to have been able to experiment on solutions obtained by mixing absolutely non-volatile substances with the ether. Unfortunately, nearly all of the substances soluble in all proportions in ether have an appreciable vapor-pressure at the ordinary temperature, and the best I could do was to select for my experiments those substances whose vapor-pressure was the smallest.

These are:

	BOILING-POINTS.
Oil of turpentine	160°
Nitrobenzene	205°
Aniline	182°
Methyl salicylate	222°
Ethyl benzoate	213°

At a given temperature the vapor-pressures of the last four substances are less than that of the oil of turpentine, which is known from the experiments of Regnault, and which, in the neighborhood of 15°, is not one-ninetieth of that of the ether. Besides, as I shall show later, they are considerably diminished in the ethereal solutions, and they do not prevent the manifestation of the general laws which govern the phenomena.

In the following tables:

The first column gives the weight, Q, of substance dissolved in 100 grams of solution. This is equal to $\frac{100\,p'}{p+p'}$, in which p' is the weight of substance mixed with a weight p of ether.

The second column gives the number, n, of molecules of substance existing in 100 molecules of the solution. This is equal to $\frac{7400 \times p'}{p' \times 74 \times pm}$, in which 74 is the molecular weight of ether, and m that of the dissolved substance.

The third column indicates the experimental value of the ratio $\frac{f'}{f}$, between the vapor-pressure of the solution f' and that of pure ether f at the same temperature. This ratio has been multiplied by 100.

The fourth column gives the values of $\frac{f'}{f} \times 100$, calculated from the formula:

$$\frac{f'}{f} = 1 - K \times \frac{74 \times p'}{74 \times p' + pm'},$$

in which the coefficient K varies with the nature of the substance dissolved in the ether.

Mixtures of Oil of Turpentine and Ether.

$C_{10} H_{16} = 136$

Temperature of the experiments..... 16°.2
Vapor-pressure of the oil of turpentine at the temperature of the experiments..... 4 mm.
Vapor-pressure of pure ether at the same temperature 377 mm.

Weights of Oil in 100 Grams of Mixture.	Number of Molecules of Oil in 100 Molecules of Mixture.	Ratio between the Vapor-Pressure of the Mixture and that of Pure Ether, Multiplied by 100, or $\frac{f'}{f} \times 100$.	
Q	N	Observed.	Calculated.
(1)	(2)	(3)	(4)
10.2	5.9	94.0	94.7
20.2	12.1	88.1	89.1
35.9	23.4	78.1	78.9
50.3	35.5	67.6	68.0
62.8	47.9	56.2	56.9
76.9	64.5	42.1	42.0

The values of $\frac{f'}{f} \times 100$, in the last column, were calculated by means of the formula:

$$\frac{f'}{f} \times 100 = 100 - 0.90 \times N.$$

This is the equation of a straight line having $\frac{f'}{f} \times 100$ for ordinates, and N for abscissae, *i. e.*, the number of molecules of substance contained in 100 molecules of the mixture.

The agreement between the results observed and calculated is as satisfactory as could be desired.

Remark.—The oil of turpentine after it has been distilled for some time soils mercury very badly. To have it in proper condition I pour a certain quantity of mercury in the flask in which it is contained, and after closing the flask I expose it to the sun, and shake from time to time. After eight days I distil over magnesium, in a condenser with two bulbs, and I use the product which passes over at 159° as soon as it is obtained.

Mixtures of Nitrobenzene and Ether.

$C_6H_5NO_2=123.$

Temperature of experiment..... 16°
Vapor-pressure of nitrobenzene at the temperature of experiment..... 2 mm.
Vapor-pressure of pure ether at the same temperature 374 mm.

Nitrobenzene, prepared from pure benzene, was purified at first by distillation. A few days before using it it was repurified by repeated crystallizations. It was nearly colorless.

Weights of Nitrobenzene in 100 Grams of Mixture.	Number of Molecules of Nitrobenzene in 100 Molecules of Mixture.	Ratio between the Vapor-Pressure of the Mixture and that of Pure Ether, Multiplied by 100, or $\frac{f}{f'}\times 100$.	
Q	N	Observed.	Calculated.
(1)	(2)	(3)	(4)
9.6	6.0	94.5	95.6
26.7	17.9	85.8	86.8
47.2	35.5	74.4	73.7
65.4	53.2	62.0	60.6
80.9	75.9	44.4	43.8
88.5	84.0	35.5	37.8

The calculated values of $\frac{f'}{f}\times 100$, in the fourth column of this table, were obtained by means of the formula:

$$\frac{f'}{f}\times 100=100-0.74\times N.$$

They evidently agree closely with those furnished by observation.

Mixtures of Aniline and Ether.

$C_6 H_7 N = 93.$

Temperature of the experiments..... 15°.3
Vapor-pressure of aniline at this temperature..... 3 mm.
Vapor-pressure of ether at this temperature ..... 364 mm.

The aniline was prepared from pure nitrobenzene and purified by distillation. It was colorless.

Weights of Aniline in 100 Grams of Mixture.	Number of Molecules of Aniline in 100 Molecules of Mixture.	Ratio between the Vapor-Pressure of the Mixture and that of Pure Ether, Multiplied by 100, or $\frac{f'}{f} \times 100$.	
Q	N	Observed.	Calculated.
(1)	(2)	(3)	(4)
4.8	3.85	96.0	96.6
9.5	7.7	91.9	93.1
18.1	14.8	84.5	86.7
24.5	20.5	80.3	81.6
55.3	49.6	57.6	55.4
73.4	68.7	40.4	38.2

The calculated values of $\frac{f'}{f} \times 100$, in the fourth column, were obtained by means of the formula:

$$\frac{f'}{f} \times 100 = 100 - 0.90 \times N.$$

They agree fairly well with the results of observation.

Mixtures of Methyl Salicylate and Ether.

$C_8 H_8 O_3 = 152.$

Temperature of the experiments..... 14°.1
Vapor-pressure of methyl salicylate at this temperature..... 2 mm.
Vapor-pressure of ether at the same temperature.... 346 mm.

Weights of Salicylate in 100 Grams of Mixture.	Number of Molecules of Salicylate in 100 Molecules of Mixture.	Ratio between the Vapor-Pressure of the Mixture and that of Pure Ether, Multiplied by 100, or $\frac{f'}{f} \times 100$.	
Q	N	Observed.	Calculated.
(1)	(2)	(3)	(4)
2.256	1.1	99.6	99.1
4.20	2.1	99.3	98.3
9.4	4.8	96.0	96.1
17.3	9.2	91.4	92.5
26.8	15.1	87.0	87.6
38.6	23.2	81.1	81.0
66.4	49.0	60.0	59.8
87.3	77.0	36.1	36.9
91.4	85.0	29.2	30.3

The calculated values of $\frac{f'}{f} \times 100$, in the fourth column, were obtained by means of the formula:

$$\frac{f'}{f} \times 100 = 100 - 0.82 \times N.$$

The agreement between the calculated and the observed results is quite remarkable.

Mixtures of Ethyl Benzoate and Ether.

$C_9 H_{10} O_2 = 150$.

Temperature of the experiments..... 11°.7
Vapor-pressure of ethyl benzoate at this temperature. 3 mm.
Vapor-pressure of pure ether at the same temperature 313 mm.

The ethyl benzoate was purified by the ordinary method. It nearly all distilled over at 213°.

Weights of Ethyl Benzoate in 100 Grams of Mixture.	Number of Molecules of Ethyl Benzoate in 100 Molecules of Mixture.	Ratio between the Vapor-Pressure of the Mixture and that of Pure Ether, Multiplied by 100, or $\frac{f'}{f} \times 100$.	
Q	N	Observed.	Calculated.
(1)	(2)	(3)	(4)
9.4	4.9	94.9	95.6
17.7	9.6	90.9	91.4
43.0	27.1	75.2	75.6
69.6	53.0	52.9	52.3
86.2	75.5	30.0	32.1
97.1	94.4	12.4	15.0

The calculated values of $\frac{f'}{f} \times 100$, in the last column, were obtained with the aid of the formula:

$$\frac{f'}{f} \times 100 = 100 - 0.90 \times N;$$

and here, also, they agree satisfactorily with the values found by experiment.

General Results.—We see that for the different mixtures studied the results obtained agree pretty well, as a whole, with the results calculated by means of the formula:

$$\frac{f'}{f} \times 100 = 100 - KN, \tag{1}$$

in which N is the number of molecules of non-volatile substance existing in 100 molecules of the mixture, and K a coefficient which depends only upon the nature of the substance mixed with the ether.

It should be observed that the coefficient K generally varies but little with the nature of the dissolved substance, and it is usually very nearly unity. Its values for the following substances are:

Oil of turpentine in ether	$K = 0.90$
Aniline in ether	$K = 0.90$
Ethyl benzoate in ether	$K = 0.90$
Methyl salicylate in ether	$K = 0.82$
Nitrobenzene in ether	$K = 0.70$

I made similar experiments on mixtures of *carbon bisulphide* with different substances as slightly volatile as the above. These experiments, an account of which will be given later, prove that the ratio $\frac{f'}{f}$ varies, in this case, with the concentration, according to the same laws as in the ethereal solutions; and that in formula (1), which sums them up, the coefficient K is also a little less than unity. This formula ought, therefore, until the contrary is proven, to be considered as applicable to the calculation of the vapor-pressures of all volatile liquids employed as solvents.

We will now avail ourselves of it to determine to what extent the preceding results are modified by the vapor-pressure of the substances mixed with the ether.

Influence of the Vapor-Pressure of the Substances Mixed with

the Ether.—Let ϕ be the vapor-pressure which the dissolved substance possessed when pure; ϕ', the vapor-pressure of the same substance when mixed with the ether; N', the number of molecules of ether in 100 molecules of the mixture.

The vapor-pressure f' of an ethereal solution, being the sum of the partial pressures of the ether and of the dissolved substance, the partial pressure of the ether vapor in the mixture is $f'-\phi$. But from formula (1), which finds here a legitimate application:

$$\phi'=\phi\left(1-\frac{KN'}{100}\right). \tag{2}$$

From this we have:

$$f'-\phi'=f'-\phi\left(1-\frac{KN'}{100}\right),$$

or in dividing by f, the tension of pure ether:

$$\frac{f'-\phi'}{f}=\frac{f'}{f}-\frac{\phi}{f}\left(1-\frac{KN'}{100}\right), \tag{3}$$

the exact value of the ratio $\frac{f'-\phi'}{f}$, which exists between the vapor-pressures of the ether in the mixture, and when pure, is obtained, therefore, by cutting off the term $\frac{\phi}{f}\left(1-\frac{KN'}{100}\right)$ from the crude ratio $\frac{f'}{f}$.

But in all of the preceding experiments the ratio $\frac{\phi}{f}$ between the tension of the dissolved substance and that of the ether, both considered as pure, is less than $\frac{1}{10}$. The correction term $\frac{\phi}{f}\left(1-\frac{KN'}{100}\right)$ is, therefore, always less than $\frac{1}{10}$, and it becomes less than $\frac{1}{180}$ for the values of N' which are greater than 50. It is, consequently, always negligible in comparison with the experimental errors. The influence of the vapor-pressure of the substances mixed with the ether is, therefore, too slight to be introduced as a correction into the results obtained.

Causes of Error in Concentrated Solutions.—There are some differences between the results observed and those calculated by formula (1), and these appear especially with very concentrated or very dilute solutions.

As far as the very concentrated solutions are concerned, in

which N is greater than 70—*i. e.*, in which there are more than 70 molecules of non-volatile substance to 100 molecules of mixture—the differences are perhaps due only to errors of experiment. The determinations then become very difficult indeed. In such mixtures the proportion of ether is very slight, and however little ether is lost by evaporation during the transfer, a loss which is inevitable, the solutions become more concentrated and their vapor-pressures too small. Moreover, it may happen that the liquid layers in contact with the vapor in the barometric tubes, become more concentrated than the deeper layers, notwithstanding the shaking; and in this case, again, their vapor-pressure would be too slight.

Laws Relating to Dilute Solutions.—For solutions which are dilute and in which N is less than 15, the differences disappear for the most part if in formula (1) K is made equal to 1. Indeed, in this case the results of experiment agree nearly always to $\frac{1}{200}$ with those given by the formula:

$$\frac{f'}{f} \times 100 = 100 - N. \tag{4}$$

To show this important fact, I give in the following table the results calculated by means of this formula (4), together with the results observed with different dilute solutions, for which $N < 15$:

SUBSTANCE DISSOLVED IN ETHER.	MOLECULAR CONCENTRATION. N.	$\frac{f'}{f} \times 100$. CALCULATED.	$\frac{f'}{f} \times 100$. OBSERVED.	DIFFERENCE.
Oil of turpentine.	5.9	94.1	94.0	$\frac{1}{940}$
	12.1	87.9	88.1	$\frac{2}{881}$
Nitrobenzene....	6.0	94.0	94.5	$\frac{5}{945}$
Aniline.....	3.85	96.2	96.0	$\frac{2}{960}$
	7.7	92.3	92.3	0
Methyl salicylate.	1.1	98.9	99.6	$\frac{7}{996}$
	2.1	97.9	99.3	$\frac{14}{993}$
	4.8	95.2	96.0	$\frac{8}{960}$
	9.2	90.8	91.4	$\frac{6}{914}$
Ethyl benzoate...	4.9	95.1	94.9	$\frac{2}{949}$
	9.6	90.4	90.9	$\frac{5}{909}$

We see that the difference between the results observed and calculated seldom exceeds $\frac{1}{200}$ of their value. There is an

exception only for extremely dilute solutions—*i. e.*, those in which N is less than 2, which seem to follow a more complicated law. But it appears to me to be hardly possible to make any assertion regarding them; determinations of this kind becoming more and more difficult and uncertain as the dilution increases.

Formula (4) is, therefore, in accord with experiment, as far as could be desired, as long as the values of N are between 2 and 15.

Comparison with the Law of Wüllner.—Different physicists, and particularly Von Babo and Wüllner, have shown that for certain solutions of salt in water the relative diminution of pressure $\frac{f-f'}{f}$ is practically proportional to the weight of salt dissolved in a constant weight of water. This can be expressed by the formula:

$$\frac{f'}{f}\times 100 = 100 - KN\times\frac{100}{100-N}, \tag{5}$$

K being a constant coefficient for each substance.

This expression differs considerably from formula (4); but it should be observed that the latter applies especially to ethereal solutions, for which $N>3$. Often when $N<3$, formula (4) applied to aqueous solutions gives results which are too large, and then formula (5) advantageously replaces it. Besides this special case, formula (5) gives, even for aqueous solutions, information which is more and more erroneous as N becomes greater. In addition, it leads to negative values for $\frac{f'}{f}$ when $N>\frac{100}{K+1}$, which is absurd.

These variations very probably result from the fact that the condition of the substance in the solutions changes with the concentration; and we ought to be astonished that, notwithstanding all this, we can express the vapor-pressure f' of the ethereal solutions by means of two relations which are also simple; the one, (1), giving the values of f' at least to about $\frac{1}{20}$, for all the values of N from 0 to 70; the other, (4), giving them to about $\frac{1}{100}$ for all the values of N between 3 and 15.

Particular Expression of the Law relating to Dilute Solutions.—Formula (4), relating to dilute solutions, acquires an interesting form if were place N by $100-N'$, the quantity N

being the number of molecules of ether contained in 100 molecules of the mixture. This formula then becomes transformed into the following:

$$\frac{f'}{f}\times 100 = N', \tag{6}$$

which is to say that, *in ethereal solutions of medium concentrations, the partial pressure of the ether vapor is proportional to the number N', of molecules of ether existing in* 100 *molecules of the mixture, and is independent of the nature of the dissolved substance.* I shall return again to the last point.

Influence of Temperature on the Vapor-Pressure of Ethereal Solutions.—To study the influence of temperature I placed four barometric tubes, containing the dilute solutions obtained by mixing different high-boiling substances with the ether, in the same mercury bath for several months. I then measured the vapor-pressure very carefully whenever the circumstances were favorable. Although in this interval the temperature varied from 0° to 22°, I always found approximately the same value for the ratio $\frac{f'}{f}$.

Some of the results obtained are collected in the following tables. t is the temperature, f the vapor-pressure of pure ether, and f' the vapor-pressure of the solution.

Mixture of 16.482 *Grams of Oil of Turpentine and* 100 *Grams of Ether.*

t	f	f'	$\frac{f'}{f}\times 100$
1°.1	199.0	188.1	91.5
3°.6	224.0	204.7	91.4
18°.2	408.5	368.7	91.0
21°.8	472.3	430.7	91.2

Mixture of 10.442 *Grams of Aniline with* 100 *Grams of Ether.*

t	f	f'	$\frac{f'}{f}\times 100$
1°.1	199.5	183.3	91.9
3°.6	223.2	204.5	91.6
9°.9	289.1	264.0	91.3
21°.8	472.9	432.7	91.5

Mixture of 27.601 *Grams of Hexachlorethane with* 100 *Grams of Ether.*

t	f	f'	$\frac{f'}{f}\times 100$
1°.0	197.0	181.3	92.0
3°.7	224.2	205.4	91.6
18°.8	418.6	280.9	91.0
21°.0	457.3	417.8	91.4

Mixture of 12.744 *Grams of Benzoic Acid and* 100 *Grams of Ether.*

t	f	f'	$\frac{f'}{f}\times 100$
3°.8	224.1	209.5	93.5
18°.4	412.6	382.0	92.6
21°.7	470.2	431.2	91.7

These tables show that for the solutions of oil of turpentine, of aniline, of hexachlorethane, the value of the ratio $\frac{f'}{f}$ does not vary more than 0.5 in 100, when the temperature changes from 0° to 21°. This variation is very slight and scarcely exceeds that often observed in two consecutive experiments, made on the same solution under the same conditions.

The variation for the solution of benzoic acid is a little greater, but this, perhaps, depends upon a chemical reaction which takes place in time between the substances mixed with one another.

It is worth observing that the influences of the vapor-pressure of the substances mixed with the ether is, even here, entirely incapable of appreciably modifying the ratio, $\frac{f'}{f}$. The quantity by which $\frac{f'}{f}$ is increased is, indeed, as indicated by formula (3):

(q) $$\frac{\phi}{f}\left(1-\frac{KN'}{100}\right).$$

But for the oil of turpentine, which is the most volatile of all, we have:

$$\frac{\phi}{f}=\frac{2}{184} \text{ at } 0°, \text{ and } \frac{\phi}{f}=\frac{4.5}{423} \text{ at } 20°.$$

Moreover, in all of these solutions we have $N > 90$ and K is approximately 1. The result is that the quantity, (q), to be subtracted from $\frac{f'}{s}$ is:

$$< 0.00108 \text{ at } 0°$$
$$< 0.00106 \text{ at } 20°;$$

that is, it is completely negligible in comparison with this ratio, which is here almost unity. It can all the more be rejected for the other solutions.

Finally, the preceding experiments show that the ratio $\frac{f'}{f}$ is independent of the temperature between 0° and 21°.

Influence of the Nature of the Dissolved Substance on the Vapor-Pressure of Ethereal Solutions.—The vapor-pressure, f', of a solution of a non-volatile substance in ether, the vapor-pressure of the pure ether, f, at the same temperature, and the number, N, of molecules of non-volatile substance existing in 100 molecules of the mixture, are, as we have already seen, united by the equation:

$$\frac{f'}{f} \times 100 = 100 - KN. \tag{1}$$

We can give to this expression the following form:

$$\frac{f-f'}{f} = \frac{KN}{100}. \tag{7}$$

The ratio $\frac{f-f'}{f}$, being what is called the *relative diminution of vapor-pressure* of the solution in question, formula (7) can be translated into ordinary language thus:

For all of the ethereal solutions of the same nature, the relative diminution of vapor-pressure is proportional to the number of molecules of non-volatile substance dissolved in 100 *molecules of the mixture.*

We have seen, also, that where the solutions are dilute, and where N is less than 15, the coefficient K is unity, and we have:

$$\frac{f-f'}{fN} = 0.01. \tag{8}$$

That is, *if we divide the relative diminution of pressure* $\frac{f-f'}{f}$ *of a dilute ethereal solution by the number, N, of molecules of*

non-volatile substance existing in 100 *molecules of the mixture, we obtain as a quotient* 0.01, *whatever the nature of this substance.*

With a view to ascertain whether this remarkable law is general, I dissolved in ether compounds taken from the different chemical groups, and chosen from those whose boiling-points are the highest; the compounds having molecular weights which are very widely different from one another; and I measured the vapor-pressures of the solutions obtained. In every case I found, as we will see, that the ratio $\frac{f-f'}{fN}$ is very nearly 0.01, as is required by formula (8).

The substances which I employed are, for the most part, well known to chemists, and it would be uninteresting to state here how they were prepared and purified. I shall, therefore, limit myself to giving some particular information in reference to the rarest of them, which are methyl nitrocuminate and cyanic acid.

The methyl nitrocuminate, $C_{22}H_{26}N_2O_4=382$, was prepared from a beautiful sample of very pure nitrocuminic acid, obtained by M. Alexeyeff. This acid was introduced into pure methyl alcohol, and a current of hydrochloric-acid gas was passed through the alcohol. When the reaction was over, the liquid was evaporated to dryness. Finally, the product obtained was purified by several crystallizations from methyl alcohol. This is a beautifully crystallized substance, of an orange-red color, giving with ether a nearly red solution. Its molecular weight, established with certainty by the cryoscopic method, is very high, and this is the reason which led me to use it.

Cyanic acid, $HOCN=43$, was prepared in the open air when it was very cold, by distilling dry and pure cyanuric acid. After filtration, it was introduced at $-3°$ into a tared vessel with thin walls which had been previously exhausted. This vessel was weighed, then broken in a known weight of very cold ether. The solution obtained was introduced into a barometric tube, and the air and gases dissolved in it were carefully extracted, always in the cold. The vapor-pressure of the solution was measured first at $-1°$. To my great surprise the ethereal solution contained in the barometric tube was not changed, even after two days, at the temperature of $+6°$, and I was able to make several determinations at this temperature which confirmed the results of the first.

Some substances, particularly those containing chlorine, notwithstanding the most careful purifications, still have the very inconvenient property of soiling mercury. To deprive them of this property it is only necessary to expose them to the sun in contact with mercury, in completely filled bottles, shaking them from time to time. Exposure for a few days generally suffices, if the light is intense.

The following table summarizes the results which were obtained at about 15°, with solutions containing from 4 to 12 molecules of non-volatile substance to 100 molecules of mixture. In this table:

Column (1) contains the names of the slightly volatile substances dissolved in the ether;

Column (2) gives the chemical formula and the molecular weight, M, of these substances;

Column (3) shows the number of molecules of substance dissolved in 100 molecules of mixture;

Column (4) contains the values of the ratio, $\frac{f-f'}{f}$, *i. e.*, the relative lowerings of vapor-pressure;

Column (5) gives the values of the quotient, $\frac{f-f'}{fN}$.

(1)	M (2)	N (3)	$\frac{f-f'}{f}$ (4)	$\frac{f-f'}{fN}$ (5)
Hexachlorethane.....	$C_2 Cl_6 = 237$	7.93	0.00288	0.0100
Oil of turpentine.....	$C_{10} H_{16} = 136$	8.95	0.0885	0.0099
Nitrobenzene.....	$C_6 H_5 NO_2 = 123$	6 00	0.1424	0.0084
Methyl salicylate.....	$C_8 H_8 O_3 = 152$	9.20	0.086	0.0094
Methyl nitrocuminate...	$C_{22} H_{26} N_2 O_4 = 382$	2.91	0.026	0.0089
Ethyl benzoate.....	$C_9 H_{10} O_2 = 150$	9.60	0.091	0.0095
Cyanic acid.....	$CNOH = 43$	4.52	0.041	0.0091
Benzoic acid.....	$C_7 H_6 O_2 = 122$	7.175	0.070	0.0097
Trichloracetic acid.....	$C_2 Cl_3 O_2 H = 163.5$	11.41	0.120	0.0105
Benzoic aldehyde.....	$C_7 H_6 O = 106$	12.98	0.132	0.0102
Caprylic alcohol.....	$C_8 H_{18} O = 130$	6.27	0.070	0.0110
Aniline.....	$C_6 H_7 N = 93$	7.66	0.081	0.0106
Mercury ethyl.....	$C_4 H_{10} Hg = 258$	9.75	0.089	0.0091
Antimony chloride.....	$Sb Cl_3 = 228.5$	4.27	0.037	0.0087
			Mean.....	0.0098

I have given, intentionally, the results relating to solutions

which were of very different concentrations, and in which N varied from 3 to 13. Notwithstanding this, the values of $\frac{f-f'}{fN}$ deviate relatively little from the mean 0.0098, and this mean is itself remarkably near to the theoretical value, which is 0.0100.

This suffices to show that formula (8) expresses, with as much accuracy as we could expect, the law of vapor-pressures of ethereal solutions, within the limits of concentration indicated.

Another Expression of the Law.—This law can be presented in still another way:

If R is the number of molecules of non-volatile substance dissolved in 100 molecules of ether, we have:

$$N=\frac{100\times R}{100+R}.$$

Substituting this value for N in (8), it becomes:

$$\frac{f-f'}{fR}=\frac{1}{100+R}. \tag{9}$$

As R decreases—*i. e.*, as the solution becomes more dilute—the ratio $\frac{f-f'}{fR}$ tends, therefore, towards 0.01, just as the ratio $\frac{f-f'}{fN}$; and experiment shows that it generally reaches this value as soon as $R=1$. We can therefore say:

If we dissolve 1 *molecule of any non-volatile substance in* 100 *molecules of ether, the vapor-pressure of the ether is diminished by a fraction of its value which is nearly constant, and approximately equal to* 0.01.

It is, indeed, in this form that I at first stated the law relating to the vapor-pressures of the ethereal solutions (*Compt. rend.*, December 6, 1886). But the statement corresponding to formula (8) is more exact and more general.

Determination of Molecular Weights.—It is possible to turn to account the preceding results in order to determine the molecular weights of only slightly volatile substances which are soluble in ether.

Let P be the weight of a relatively non-volatile substance dissolved in 100 grams of ether; 74, the molecular weight of ether; M, the molecular weight of the dissolved substance; N, the number of molecules of non-volatile substance dissolved in 100 molecules of mixture.

We have:

$$\frac{N}{100} = \frac{74 \times P}{100 \times M + 74 \times P}.$$

Substituting this value of $\frac{N}{100}$ in (4), it becomes, when finally transformed:

(10) $$M = 0.74 \times \frac{f' P}{f - f'} \times \ldots$$

for the molecular weight, M, of the substance dissolved in the ether.

It is clear that the value of M, thus calculated, can be only approximate. But if the boiling-point of the dissolved substance is higher than 140°, this value is always sufficiently close to the true value to determine the choice between several possible molecular weights. It is not even necessary for this purpose that the solutions be very dilute; and we always obtain results which are sufficiently exact, observing only this condition, that the weight, P, of substance dissolved in 100 grams of ether is not greater than 20 grams.

Below are some examples, taken at random, which give an idea of the degree of approximation usually reached by this process:

Oil of Turpentine.

In one experiment I had:

Weight, P, of oil (100 grams of ether)..... 11.346 gr.
Vapor-pressure of the solution f'..... 360.1 mm.
Difference between the vapor-pressure of ether and that of the solution $f - f'$..... 22.9 mm.

These values introduced into formula (10) gave:

$$M = 132.$$

But we know that the true value of M for oil of turpentine is 136. The difference is only 1 in 34.

Aniline.

Weight, P, of aniline in 100 grams of ether..... 10.442 gr.
Vapor-pressure of the solution f'..... 210.8 mm.
Difference between the vapor-pressure of ether and that of the solution $f - f'$..... 18.8 mm.

from which: $M = 87$,

a value which is nearer to the true molecular weight, 93, than to any other possible value.

Ethyl Benzoate.

Results of experiment:

$$P = 21.517 \text{ gr.}$$
$$f' = 284.5 \text{ mm.}$$
$$f - f' = 28.6 \text{ mm.}$$

Result: $M = 159.2$,

which differs from the true molecular weight, 150, by 1 part in 15.

Benzoic Acid.

Results of experiment:

$$p = 12.744 \text{ gr.}$$
$$f' = 382.0 \text{ mm.}$$
$$f - f' = 28.9 \text{ mm.}$$

from which: $M = 124.6$,

instead of 122, which is the exact molecular weight.

We see from these examples, that by observing the vapor-pressure of an ethereal solution, we can easily ascertain which of several possible values is the true molecular weight of a substance.

I do not believe, however, that it is often advantageous to have recourse to this new means of determining molecular weights. It is, indeed, rather delicate to carry out, and is successfully applicable only to substances which boil above 140°. Besides, the *cryoscopic** method, based on the observation of the freezing-point of solutions in water, in acetic acid, or in benzene, furnishes a means of arriving at the same result, which is incomparably easier, more exact, and more general. It is, therefore, only in the exceptional case that the substance under consideration is insoluble in acetic acid and soluble in ether that it is, perhaps, expedient to make use of the method based on the measurement of the vapor-pressure of ethereal solutions.

I shall show in a subsequent paper that the same laws apply to the vapor-pressure of all volatile liquids, whatsoever, employed as solvents, also to the volatility of the dissolved substance itself, and I shall deduce from them the particular laws relating to the vapor-pressures of mixtures of two volatile liquids.

* *Compt. rend.*, Nov. 23, 1885; *Ann. Chim. Phys.*, [6], **8** (July, 1886).

[E GENERAL LAW OF THE VAPOR-PRESSURE OF SOLVENTS

BY

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(*Comptes rendus*, **104**, 1430, 1887)

THE GENERAL LAW OF THE VAPOR-PRESSURE OF SOLVENTS *

BY

F. M. RAOULT

THE molecular lowering, K, of the vapor-pressure of a solution—*i. e.*, the relative diminution of pressure produced by one molecule of non-volatile substance in 100 grams of a volatile liquid—can be calculated from the following formula:

$$K=\frac{f-f'}{fP}\times M,$$

in which f is the vapor-pressure of the pure solvent, f' that of the solution, M the molecular weight of the dissolved substance, P the weight of this substance dissolved in 100 grams of the solvent; on the assumption that the relative diminution of pressure, $\frac{f-f'}{f}$, is proportional to the concentration. Since this proportionality is seldom rigid, even when the solutions are very dilute, I have endeavored in these comparative studies to always work on solutions having nearly the same molecular concentration, and containing from 4 to 5 molecules of non-volatile substance to 100 molecules of volatile solvent. A greater dilution would not permit of measurements which are sufficiently exact. All of the experiments were carried out by the barometric method, and conducted like those which I made on ethereal solutions. (*Compt. rend.*, 16 Dec., 1886.) The tubes were dipped into a water-bath with parallel glass sides, constantly stirred, and heated at will.

In each case the temperature was so chosen that the vapor-pressure of the pure solvent was about 400 millimetres of mercury. The measurements were completed in from fifteen to

* *Compt. rend.*, **104**, 1430 (1887).

forty-five minutes after stirring the contents of each tube, the temperature being constant.

I employed as solvents twelve volatile liquids — water, phosphorus trichloride, carbon bisulphide, tetrachlormethane, chloroform, amylene, benzene, methyl iodide, ethyl bromide, ether, acetone, and methyl alcohol.

I dissolved *in water* the following organic substances: Cane-sugar, glucose, tartaric acid, citric acid, and urea. All of these substances produced nearly the same molecular lowering of the vapor-pressure: $K=0.185$. I have omitted here the mineral compounds; the action of these substances has, indeed, been determined by experiments which are sufficiently numerous and conclusive, carried out by Wüllner (*Pogg. Ann.*, **103** to **110**, 1858–1860), by myself (*Compt. rend.*, **87**, 1878), and, very recently, by M. Tammann (*Wied. Ann.*, **24**, 1885).

In solvents other than water I have dissolved substances as slightly volatile as possible, and have generally chosen them from the following: oil of turpentine, naphthalene, anthracene, hexachlorethane (C_2Cl_6), methyl salicylate, ethyl benzoate, antimony trichloride, mercury ethyl, benzoic, valeric, trichlor-acetic acids, thymole, nitrobenzene, and aniline. The error due to the vapor-pressure of these compounds can often be neglected. The vapor-pressure of dissolved substances is, indeed, considerably reduced by mixing them with a large excess of solvent; and if, at the temperature of the experiment, the vapor-pressure does not exceed 5 to 6 millimetres, it does not exert any perceptible influence on the results.

The molecular lowerings of vapor-pressure, produced by these different substances in a given solvent, are grouped about two values, of which the one, which I call *normal*, is twice the other. This normal lowering is always produced by the simple hydrocarbons, and chlorides, and by the ethers; the abnormal lowering almost always by the acids. There are, however, solvents in which all of the dissolved substances produce the same molecular lowering of vapor-pressure; such, for example, as ether (*loc. cit.*) and acetone.

Of the volatile solvents examined, I have studied carefully the lowering of the freezing-point of two—water and benzene (*Compt. rend.*, **95** to **101**, and *Ann. Chim. Phys.*, [5], **28**, [6], **2** and **8**). A comparison of the results obtained shows that *for all of the solutions in a given solvent there is nearly a*

constant ratio between the molecular lowering of the freezing-point and the molecular lowering of the vapor-tension. This ratio in water is 100, in benzene 60 within $\frac{1}{20}$.

If we divide the molecular lowering of vapor-pressure, K, produced in a given volatile liquid, by the molecular weight of this liquid, M', the quotient, $\frac{K}{M'}$, represents the relative lowering of pressure which will be produced by 1 molecule of non-volatile substance in 100 molecules of volatile solvent. I have obtained the following results by making this calculation for the *normal* values of K, produced in the different solvents by organic compounds and non-saline metallic compounds:

Solvent.	Molecular weight of solvent.	Normal molecular lowering of pressure.	Lowering of pressure produced by 1 mol. in 100 mols.
	M'	K	$\frac{K}{M'}$
Water	18	0.185	0.0102
Phosphorus trichloride	137.5	1.49	0.0108
Carbon bisulphide	76	0.80	0.0105
Tetrachlormethane	154	1.62	0.0105
Chloroform	119.5	1.30	0.0109
Amylene	70.0	0.74	0.0106
Benzene	78.0	0.83	0.0106
Methyl iodide	142.0	1.49	0.0105
Ethyl bromide	109.0	1.18	0.0109
Ether	74.0	0.71	0.0096
Acetone	58.0	0.59	0.0101
Methyl alcohol	32.0	0.33	0.0103

The values of K and of M', recorded in this table, vary in the ratio of 1 to 9; notwithstanding this, the values of $\frac{K}{M'}$ vary but little, and always remain close to the mean, 0.0105.

We can therefore say that 1 *molecule of a non-saline, non-volatile substance, dissolved in* 100 *molecules of any volatile liquid, lowers the vapor-pressure of this liquid by a nearly constant fraction of its value—approximately* 0.0105.

This law is strictly analogous to that which I stated in 1882, relative to the lowering of the freezing-point of solvents. The

anomalies presented are explained, for the most part, by assuming that in certain liquids the dissolved molecules are formed of two chemical molecules.

FRANÇOIS MARIE RAOULT was born May 10, 1830, at Fournes, Nord. He was for a time professor of chemistry at the Lyceum at Sens, but was called to the professorship of chemistry at Grenoble in 1867—a position which he still holds.

His best-known work is that which has to do with the depression of the freezing-points of solvents by dissolved substances, and the lowering of the vapor-tension of solvents by substances dissolved in them. In addition to the papers given in this volume, the following may be mentioned as among his more important contributions to science:

The Law of the Freezing-Point Lowering of Water produced by Organic Substances (*Ann. Chim. Phys.*, [5], **28**, 133, 1883); *On the Freezing-Point of Salt Solutions* (*Ann. Chim. Phys.*, [6], **4**, 401, 1885; *On the Vapor-Tension and Freezing-Point of Salt Solutions* (*Compt. rend.*, **87**, 167, 1878); *Law of the Freezing-Point Lowering of Benzene produced by Neutral Substances* (*Compt. rend.*, **95**, 188, 1882); *General Law of the Freezing of Solvents* (*Compt. rend.*, **95**, 1030, 1882); *Determination of Molecular Weights by the Freezing-Point Method* (*Compt. rend.*, **101**, 1058, 1885); *On an Accurate Freezing-Point Method, with Some Applications to Aqueous Solutions* (*Ztschr. Phys. Chem.*, **27**, 617).

Our knowledge of the depression of the freezing-point and of the vapor-tension of solvents by dissolved substances, was fragmentary before the time of Raoult. He was the first to discover the general laws to which these phenomena conform—laws which have an important bearing on chemistry and physics, and which are especially significant for the physical chemist.

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